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# Quantum-chemical Calculations in the Study of Antitumour Compounds

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The results of quantum-chemical calculations on antitumour preparations concerning the mechanism of their action at the electronic and molecular levels and structure-activity correlations are discussed in this review. Preparations whose action involves alkylating and free-radial mechanisms, complex-forming agents, and antimetabolites are considered. Modern quantum-chemical methods for calculations on biologically active substances are described.
The bibliography includes 106 references.

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## 1. INTRODUCTION

The wide-scale employment of the ideas and methods of chemical kinetics and physical organic chemistry in experimental and clinical oncology have led to the creation of a new field of fundamental and applied research—the physical chemistry of cancer, founded by Academician N.M.Emanuel'.[1,2] In relation to the current problems of tumour chemotherapy, these approaches have been directed towards the study of the relation between the structure and chemical reactivity of antitumour compounds (ATC) on the one hand, and their biological effects on the other. ATC are distinguished from other types of medicinal preparations by including representatives from different classes of chemical compounds. For this reason, the antitumour effect of the preparations at the molecular level cannot be accounted for in terms of a single mechanism of their action.

Fundamental principles governing the creation of new effective antitumour preparations, which have been developed by Emanuel', include the classification of ATC in terms of their chemical reactivities.[3,4] This classification constitutes the basis of the study of the anticancer preparations at the electronic and molecular levels and the establishment of quantitative structure—activity correlations, in which quantum-chemical calculations play an important role.[4]

Modern quantum-chemical methods are widely used in studies on biomacromolecules and biologically active compounds (BAC). Recently ATC have also begun to be actively investigated by these methods. Whereas in 1976 the lack of information about calculations for ATC was noted in Pullman's monograph[5] on quantum-chemical calculations of the conformations of medicinal preparations, by 1984 several tens of articles devoted to quantum-chemical studies on preparations of this kind were already published in the world scientific

literature. This review contains information about quantum-chemical calculations of the electronic parameters of ATC molecules and about the modelling of the mechanisms of their biological action at the electronic and molecular levels.

## II. CHARACTERISTIC FEATURES OF THE USE OF QUANTUM-CHEMICAL METHODS IN THE STUDY OF BIOLOGICALLY ACTIVE COMPOUNDS

### 1. Quantum-chemical Calculations of the Electronic Structure

According to the postulates of quantum mechanics, the structure and properties of the molecule can be determined from its wave function $\Phi$. The wave function is found by solving the fundamental quantum-mechanical equation—the Schrödinger equation. As a result of the development of computer techniques, fairly accurate methods have been devised in modern quantum chemistry whereby the Schrödinger equations can be solved for the stationary states of many-electron and polyatomic systems to which BAC belong. Quantum-chemical methods in which $\Phi$ is formulated as an antisymmetrised product of the spin orbitals whose coordinate components (MO) are represented by linear combinations of atomic orbitals (LCAO) have come to be most widely employed in studies on BAC. The positions of the nuclei are assumed to be frozen (adiabatic approximation). The quantum-mechanical calculation reduces to finding the coefficients of the expansion of the MO in terms of the AO by solving the Hartree–Fock–Roothaan equations, which consist of a system of algebraic equations. Several monographs on the principles of quantum chemistry have now been published[6-9] and a more detailed exposition of questions concerning the computational methods, which are only briefly described here, may be found in them.

The quantum-chemical calculation yield information about the spatial distribution of electrons in the molecule and about the energy levels of the electrons. The total energy of the system includes contributions by the one-electron orbital energies and the integrals of the Coulombic and exchange interactions. Despite the approximations underlying it (in particular the neglect of the correlation energies of electrons), the application of the Hartree–Fock–Roothaan method makes it possible to estimate fairly accurately many phyisochemical characteristics of many-electron molecules. Depending on the approaches to the solution of the Hartree–Fock–Roothaan equations used, the quantum-chemical methods are divided into non-empirical (*ab initio*) and semiempirical.

The non-empirical methods are based on a rigorous solution of the Hartree–Fock–Roothaan equations. In the calculations account is taken of all the electrons in the molecule and of all the interelectron interaction integrals. An important feature of the *ab initio* calculations is the choice of the form of the AO basis set in terms of which the MO are expanded. Various representations of the AO in the form of Gaussian functions are used nowadays for calculations on polyatomic molecules. The total energy in non-empirical calculations using different selections of the AO basis set varies within the limits of several per cent relative to its lower limit attainable by the one-determinant Hartree–Fock method.[8] However, the accuracy of the calculation of the physical properties depends very greatly on the choice of the AO basis set. It has been noted in a review[10] that, for a correct calculation of the molecular geometry and the orbital energies (for example, for comparison with photoelectron spectra), it is sufficient to employ a minimal basis set; the calculation of the isomerisation energies and conformational properties requires the use of a two-exponent basis set; for the calculation on negatively charged ions and excited states, it is essential to employ a two-exponent basis set with allowance for diffuse orbitals; the exact calculation for van der Waals interactions, spin densities, and magnetic permeabilities makes it necessary to abandon the one-determinant approximation and to employ the multiconfiguration Hartree–Fock method with a basis set of two-exponent and polarisation functions.

The increase in the complexity of the sets of basis functions entails a sharp decrease in the molecular size susceptible to calculation, which is due to the increase in computing time required to evaluate the electronic integrals and to the limited capacity of the operating memory and the peripheral memory devices of the computer. For this reason the simplest possible basis sets are used for calculations on BAC,[11] the minimal STO-3G basis set being widely employed. Non-empirical calculations for a wide range of organic compounds in terms of this basis set reliably reproduced the equilibrium geometry of neutral molecules, the heats of atomisation, the dipole moments, and the molecular electrostatic potentials.

Much attention has been devoted recently to the development of *ab initio* methods disigned for the direct investigation of large molecules.[12] The computational aspects of the non-empirical calculations have in this instance certain unusual features; in particular, owing to the large interatomic distances within the molecule, there is a possibility of an appreciable diminution of the number of two-electron integrals differing appreciably from zero. It has been suggested that the number of integrals considered be reduced by a rigorous consideration of only the valence electrons and the employment of a model potential (MODPOT) for the electrons of the skeleton,[13] by variable [partial] retention of [diatomic] differential overlap (PRDDO;[14] VRDDO [15]), and by the ruse of the integrals for similar strucual fragments (MERGE).[16] It has been noted that, when the very latest CRAY computers with a vector processor are used, the integrals are calculated so rapidly that it becomes reasonable to recalculate them anew each time instead of reading them from a peripheral memory device.[17] In this case the computer memory stores several sets of indices of non-zero integrals. Such "approximate" non-empirical methods, whose accuracy differs little from that of the calculations in terms of the STO-3G basis set, permit an appreciable saving in computing time—VRDDO by 25%, VRDDO/MODPOT by a factor of 3, and PRDDO by a factor of 15 compared with STO-3G.[18] The gain in time increases with increase of the number of AO. The employment of the PRDDO and VRDDO methods is apparently optimal (in relation to the accuracy/computing time ratio) in calculations on BAC.[18]

Despite the endeavour to employ rigorous non-empirical methods, various approximate methods for finding the wave functions, referred to as semiempirical methods, arose in the course of the development of quantum chemistry. Their appearance is associated with the methodological and technical difficulties which occurred and still occur in rigorous *ab initio* calculations. In the semiempirical methods the Hartree–Fock–Roothaan equations are solved subject to a series of approximations in the formulation of the Hamiltonian, which are based on the allowance for the interaction of only some of the electrons of the molecule (electrons or valence electrons) and the neglect of some of the inter-electron repulsion integrals. The introduction of such approximations is compensated by employing, in constructing the Hamiltonian, semiempirical parameters selected on the basis of experimental data. By means of a correct choice of parameters in the semiempirical method, it is possible to reproduce correctly in qualitative terms certain physicochemical properties of the molecules and, in particular, their variation in series of related compounds. However, as a result of the loss of rigour in the treatment, certain molecular characteristics and

intermolecular interaction energies reproduced by the semiempirical methods are in principle incorrect. Therefore the use of semiempirical calculations makes it necessary to estimate in each case the scope of the approach selected for the solution of the given problem.

Computer programmes now exist for a whole series of different quantum-chemical methods which form a virtually continuous spectrum between simple schemes with complete neglect of differential overlap (CNDO) and rigorous *ab initio* approaches. The following approaches are employed most frequently in quantum biochemistry: different versions of the Hückel method, methods of the CNDO type (CNDO/2, CNDO/BW, CNDO/S), INDO, INDO/S, MINDO/2, MINDO/3, MNDO, VRDDO, and the *ab initio* STO-3G method. In the above list the methods are arranged in order of increasing rigour of the treatment of the Hartree–Fock–Roothaan equations. The practical choice of the method is usually dictated by its feasibility as regards its application on a given computer and by the character of the problem. In the USSR there is a library of quantum-chemical programmes (analogous to the library of QCPE computer programmes available in the USA),[19] which apply the majority of standard semiempirical and non-empirical methods. The programmes are designed for computers of the BESM-6 type, which remain the most widely used in scientific centres, and EC. A detailed comparison of the characteristics of Soviet and foreign computers and their scope as regards the solution of quantum-chemical problems may be found in the book of Shchembelov et al.[9]

## 2. Analysis of the Reactivities of BAC

In the first stage of a quantum-chemical study, one selects and determines the molecular structure of the test compound. Data on molecular structure can be obtained experimentally (by the X-ray diffraction and spectroscopic methods and by gas electron diffraction). In many cases such structural information is subsequently used directly to calculate the wave function. In those cases where experimental data are lacking or are incomplete, the equilibrium molecular structure is calculated by a quantum-chemical method. For this purpose, the total energy of the molecule, which is a function of the structural parameters (the atomic coordinates or the generalised coordinates), is minimised with respect to these parameters. The use of gradient optimisation methods in combination with an adequate choice of the methods for the calculation of the wave function itself, usually gives rise to a satisfactory quantitative agreement with experiment.[8] The conformational analysis of the BAC also constitutes a separate problem, which is important for the elucidation of the specific features of their interaction with receptors and for the synthesis of new medicinal drugs.[20]

The reactivities of BAC are usually analysed by considering the reactivity indices (RI). These are defined as the molecular characteristics, calculated quantum-chemically, from which one can infer the occurrence of a specific chemical reaction. A simple physical characteristic of the molecule can serve as an index of this kind. The expected value of such a physical property $M$ is calculated, in conformity with the postulates of quantum chemistry, by the formula

$$M = \int \Phi \hat{M} \Phi^* dV ,$$

where $\hat{M}$ is the corresponding $M$ operator and $\Phi^*$ is the complex conjugate of the wavefunction $\Phi$, and the integration is carried out over all the variables in $\Phi$. The characteristics which depend solely on the properties of the isolated molecule determine the changes in the electronic structure of the molecule at an early stage of the reaction and they are referred to as the static RI. The parameters which take into account the mutual influence of the reactants describe the properties of the molecule at an intermediate stage of the reaction and are referred to as the dynamic RI. The RI permit only a relative conclusion, i.e. they make it possible to infer the variation of reactivity in a series of related compounds. The main condition governing the applicability of the RI is that the principle of the linear variation of the free energies holds for the given series at all stages of the reaction, which means that, when the energies of the initial reaction stage for a series of $n$ compounds are arranged in the sequence $E_1E_2...E_n$, then this same sequence should hold also subsequently.

The principal RI characterising the energetic and structural parameters of molecules as well as the corresponding physicochemical (including spectroscopic) properties of the molecules are presented below (Fig.1).

The majority of the indices quoted are static. The significance of a particular index in each case is determined by the nature of the process investigated. In the case of a bimolecular reaction the overall expression for the energy of the interaction of the reactants $E_t$ can be obtained from perturbation theory:[8]

$$E_t = E_Q + E_{ind} + E_{ex} + E_{ct} + E_{disp} ,$$

where $E_Q$ is the energy of the Coulombic interaction, $E_{ind}$ the energy of the inductive interaction, $E_{ex}$ the energy of the exchange interaction, $E_{ct}$ the energy of the charge transfer interaction, and $E_{disp}$ the energy of the dispersion interaction. The total energy $E_t$ is itself the most general dynamic RI. The formulae for the different contributions to $E_t$ have been published.[8] When the reaction depends at some stage mainly on interactions of one kind, the expression which can be fitted to the corresponding interaction may serve as a satisfactory dynamic index. In such cases it is frequently possible to isolate also the static RI on the basis of which one can predict the reactivity in the series of substances investigated. For example, electrostatic interactions play an important role in the formation of hydrogen-bonded complexes and the corresponding index, the molecular electrostatic potential (MEP), is satisfactorily correlated with the total energy of the hydrogen bond.

The quantum-chemical analysis of the reactivities of BAC is nowadays performed in most cases for isolated molecules. Such models correspond to gas-phase reactions and the feasibility of transferring the results of calculations for such reactions to liquid-phase biological processes requires additional justification. According the Reichardt[21] the solvent exerts a stronger influence on the reactions in which the transition state of the molecule has a dipolar structure. The polarity of the solvent is then of decisive importance. In cases where the transition state is not characterised by an isopolar or free-radical structure, the influence of the solvent is small. In calculations of reactivities in such cases one can apparently restrict the treatment to the approximation of an isolated molecule. The solvent influences the conformational characteristics and the reactivity both via its macroscopic properties (dielectric constant, surface tension) and via specific solvation in which the strong interaction (hydrogen bonding, the formation of a π-complex) between the solvent and solute molecules is important. These effects are taken into account in quantum-chemical calculations within the framework of "continuous" models and "supermolecular" models,[22] but the methodological difficulties associated with allowance for solvation effects remain one of the problems in quantum chemistry.

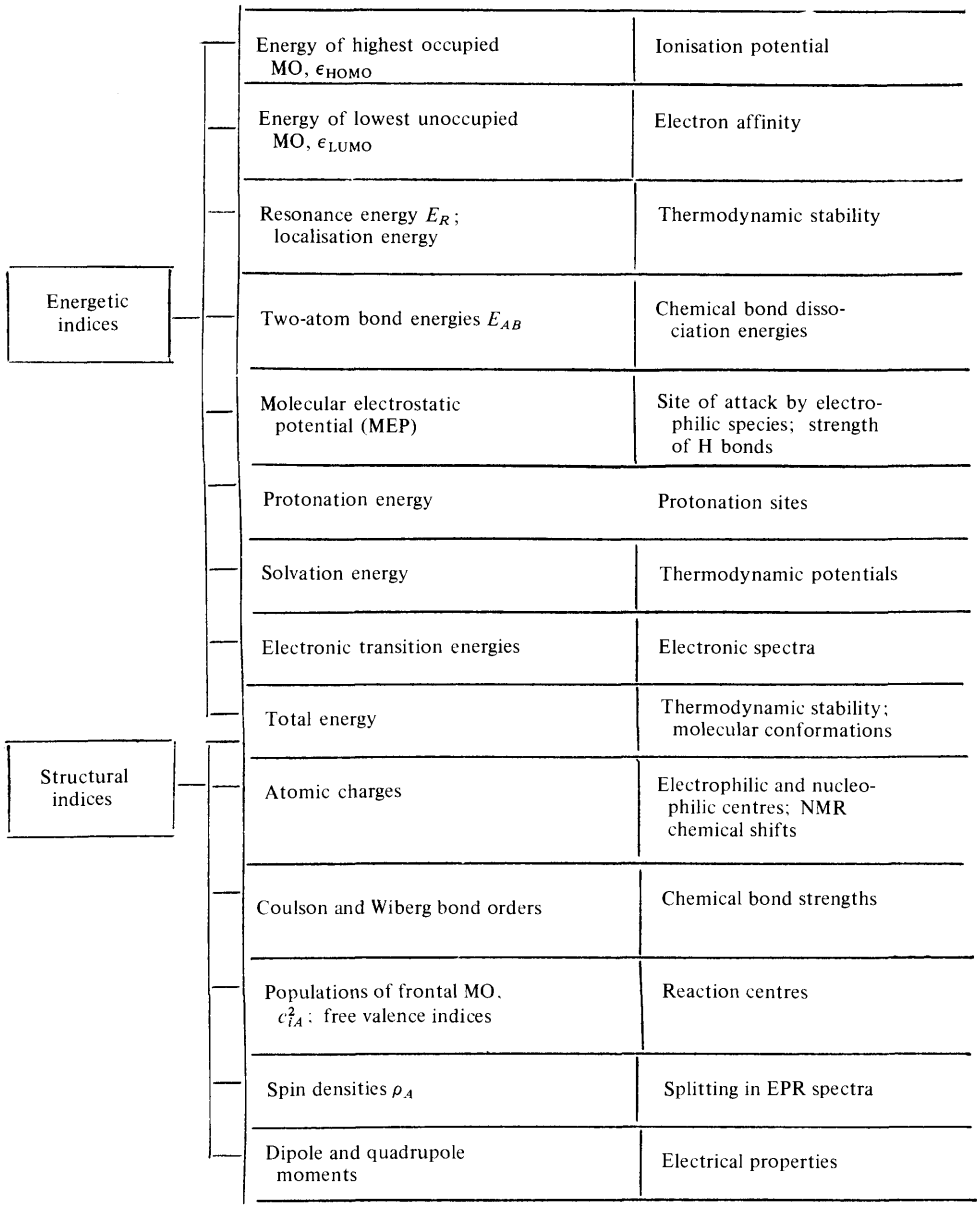



**Figure 1.** The reactivity indices used in the study of BAC and their physicochemical interpretation.

### 3. Statistical Structure–Activity Relations

The parameters of the electronic structure carry direct information only about chemical reactivity. In order to reach conclusions of a biological character, it is necessary to trace the relation between the RI (chemical interaction) and the biological effect of the compound. Quantum-chemical calculations sometimes make it possible to put forward a hypothetical model of the biological activity of just one preparation on the basis of the analysis of experimental data for its biological activity. However, it is more usual to calculate the electronic parameters for a series of compounds with similar structures for which the quantitative characteristics of the biological effects investigated are known, and then the question of the existence and nature of quantitative structure–activity correlations (QSAC) is investigated.[23,24] QSAC are usually analysed in terms of Hansch's model,[25] in which the rate of the biological response $k_{br}$ is represented in the form

$$k_{br} = Ack_r,$$

where $A$ is the probability that the BAC molecule reaches the receptor, $c$ the extracellular concentration of the BAC, and $k_r$ the rate of reaction between the BAC and the receptor. The biological effectiveness is determined by the concentration $c$ necessary to attain a specified level $k_{br} = \text{const}$.

A Gaussian relation governing the lipophilicity coefficient $\pi$, namely

$$\pi = \lg P_s - \lg P_0 ,$$

where $P_S$ and $P_0$ are the partition coefficients between water and octanol (octanol is used as the model of a lipid) of the given ($s$) and initial (0) compounds, is used for the quantity $A$ characterising the transition from the aqueous phase via the lipid membrane into the cell. The rate $k_r$ is determined from the Hammett equation $k_r = \rho\sigma$. The final equation relating $c$ to the parameters of the compound is

$$\lg(1/c) = K_1\pi - K_2\pi^2 + \rho\sigma + K_3 , \quad (1)$$

where $K_1$, $K_2$, and $K_3$ are constants found by regression analysis. In many cases it is possible to restrict the treatment to the consideration of only the linear terms of Hansch's equation. Such regression relations are also used with parameters of other types, for examples, those of the Free–Wilson and Cammarata models.[26–28] None of these models presuppose quantum-chemical calculations. However, it is now recognised that quantum-chemical RI offer greater possibilities for the analysis of structure–activity relations.[23,24]

A direct relation has been traced between the hypotheses underlying Hansch's equation and the condition governing the applicability of the RI. In each case it is then as a rule possible to select quantum-chemical parameters which are more effectively correlated with the $k_r$ than the Hammett constants. This has been responsible for the wide-scale application of RI in deriving relations of type (1). Numerous different simple static RI are used nowadays in QSAC. This hinders regression analysis and yields little information about the mechanism of the action of the preparation. It has been suggested[29] that statistically independent linear combinations of RI (principal components) be employed. Such an approach simplifies the statistical treatment but makes it difficult to interpret the mechanism of the action of the given compound. In our view the reliability of QSAC should be improved by employing complex dynamic RI which are more effectively correlated with the $k_r$.

The transport properties of chemotherapeutic preparations, which depend both on the structural-functional characteristics of the ATC (molecular size, p$K$, and lipophilicity) and on the rate of blood flow, the permeability of cytoplasmic membranes, the rate of biotransformation etc., are important for the manifestation of the antitumour activity of such preparations.[30] The transport of chemicals across biological membranes diminishes with increase of the degree of ionisation and the molecular weight passes through an extremum (as a rule a maximum) as a function of the lipophilicity parameter $\pi$.[31] In view of its complexity, the real picture of the pharmacokinetic behaviour of the ATC in the organism and in the cell is very difficult to calculate theoretically. Hansch's equation reflects only the dependence of the biological response on the transport of the ATC across the membrane, which is in its turn specified as a function of the hydrophobic properties alone.

The experimental values of $\pi$ are as a rule used in QSAC. Theoretical estimates of $\pi$ are usually obtained with the aid of empirical additive schemes for series of related compounds.[32,33] The hydrophobic properties of the preparation can be inferred approximately also from quantum-chemical calculations for intermolecular interactions. A direct calculation of $\pi$ from the thermodynamic characteristics of the solute, evaluated by the CNDO/2 method, has been carried out for the conformers of prostaglandins.[34] A method has been proposed[35] for estimating $\pi$ from the charge distribution and the hyperconjugation indices of the isolated molecule. The fact that, according to thermodynamic equations, $\pi$ is proportional to the difference between the free energies of the substance dissolved in water and in the lipid phase can also be used in estimating the lipophilicity parameter. Qualitative agreement between the behaviour of $\pi$ and the hydration energies calculated in the electrostatic approximation using the MEP on the van der Waals surface of the molecule has been achieved[36] for a series of sterically hindered phenols.

Thus information about the electronic and molecular mechanisms of the action of the preparation can be obtained and new chemical structures with a potentially high activity can be synthesised on the basis of "quantum-chemical parameters–activity" correlations. Questions concerning the strategy of the employment of quantum-chemical calculations in the study of BAC were described previously in a series of reviews.[23,24,37] Detailed information about the mathematical methods whereby one can seek the relation between biological activity and chemical reactivity has been published.[38]

## III. QUANTUM-CHEMICAL CALCULATIONS AND THE CHEMICAL MECHANISMS OF THE ACTION OF ANTITUMOUR PREPARATIONS OF DIFFERENT CLASSES

Antitumour preparations have come to be divided into classes as a function of their chemical nature, their origin, or the mechanism of their action. The classification[39] in which the ATC are divided into (1) alkylating agents, (2) antimetabolites, (3) various synthetic preparations, (4) medicinal drugs of natural origin (antibiotics, plant preparations, enzymes), and (5) hormonal preparations is widely used.

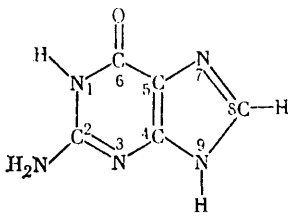
The classification of antitumour preparations in terms of the principle of chemical reactivity has been proposed by Emanuel'.[3,4] In this classification the ATC are divided into biochemically functionally active (analogues of compounds involved in cell metabolism) and chemically functionally active (characterised by a purely chemical interaction with cell molecules). The chemically functionally active ATC known at the present time are in their turn divided into groups in accordance with the chemical reactions which determine their antitumour activity. Here one encounters three main types of reactions: electrophilic reactions, complex formation, and free radical reactions. ATC with a combined mechanism of their action apparently also exist. In view of the latter factor, certain preparations, for example, the antitumour anthracycline antibiotics and sterically hindered phenols, cannot be at present assigned to a specific class. However, the classification in terms of the types of reactivity is more logical than others and can serve as a basis for the purposeful search for chemical compounds with a high antitumour activity. The results of quantum-chemical calculations on the ATC are presented below in conformity with their subdivision on the basis of their chemical reactivities.

### 1. Alkylating Agents

Alkylating compounds constitute an appreciable fraction of the antitumour agents known at the present time. Among the 58 preparations used and adopted for tests in the USSR and the USA and quoted in a monograph,[40] 23 exhibit an alkylating activity. In the course of metabolic reactions, such compounds form electrophilic species (carbonium ions), which are capable of alkylating DNA and enzymes, deactivating them thereby. The interest in alkylating agents as antitumour agents is associated with the hypothesis that the DNA in the vigorously dividing tumour cells is more susceptible to chemical action than in the normal cells at rest.

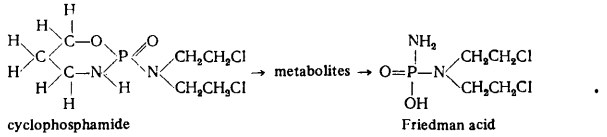
Many alkylating ATC exhibit simultaneously carcinogenic properties (the final effect of the preparation depends on the dose administered). For this reason, the conclusions and data concerning the reactivity of alkylating carcinogens are applicable to the alkylating ATC. The mechanisms of the reactions between the absolute chemical carcinogens (activated forms of carcinogens) and DNA have been examined in a review.[41] The authors note that only a small fraction of the reactions of the alkylating agents with the sites of nucleophilic attack in the DNA bases can proceed via the $S_N1$ mechanism. The $S_N2$ mechanism is commonest. Nucleic acids are alkylated to a greater extent by methylating agents than by ethylating agents. A satisfactory correlation has been observed between the carcinogenic activity of the compounds and the extent of the damage induced by them in the steric structure of the double helix of DNA.

The mechanism of the reactions of the carbonium ions $CH_3^+$ and $C_2H_5^+$ with guanine has been investigated by the non-empirical VRDDO method.[42] Potential surfaces for the reaction involving the addition of $CH_3^+$ (in the planar and pyramidal conformations) to guanine via the O[C(6)] and N(7) atoms have been calculated.



According to calculations, the attack on N(7) is preferable. The potential curves for the planar and pyramidal forms of $CH_3^+$ intersect at a distance of 3.7 a.u. from guanine. The intersection of the curves is due to the fact that, as it approaches guanine, the planar structure becomes less stable than the pyramidal structure. There are fundamental differences between the descriptions of the methylation and ethylation reactions of the DNA bases. The ionisation potential of $CH_3^+$ ($IP$ = 9.84 eV)[42] is higher than the ionisation potentials of the DNA bases, while the opposite is true of the ionisation potential of $C_2H_5^+$ ($IP$ = 8.38 eV). Because of this, account must be taken of the mixing of the wave functions for states with transfer of $e^-$, i.e. of configuration interaction, for a correct treatment of reactions of the type $A^+ + B$ in the case of $CH_3^+$. On the other hand, calculation for the reactions of the DNA bases with $C_2H_5^+$ can also be performed in terms of the one-determinant approximation.

A considerable proportion of alkylating agents contain the mustard gas group $N(CH_2CH_2Cl)_2$. The alkylating effect of this group is associated with the formation of a carbonium ion following the elimination of a Cl atom. Cyclophosphamide belongs to the class of widely used ATC of this kind:




The cyclophosphamide metabolites and not the cyclophosphamide itself are active in the organism. The atomic mechanism of the alkylating activity of cyclophosphamide has been investigated.[43-45] The author took into account the influence of the low-lying singlet ($S_n^*$) and triplet ($T_n^*$) excited levels on the reactivity of the ground state. The excited states play an important role in the study of dark reactions between molecules in view of their involvement in intramolecular and intermolecular charge transfer processes and spin–orbital interactions. The energies of the excited levels have been calculated by the CNDO/S method taking into account the interaction of singly excited configurations. The contribution due to the overlap of diffuse 3*d* AO of the P atom with the AO of all the atoms in the molecule was revealed by the calculations. In particular, the dipole moments of the transition between the excited levels are determined mainly (to the extent of 90%) by the interaction of 3*p* and 3*d* AO of P and 3*p* AO of Cl. The RI of the ground state (the charges and free valences on the atoms) differ little for cyclophosphamide and its metabolites—4-hydroxycyclophosphamide, 4-oxocyclophosphamide, aldophosphamide, carboxyphosphamide, and Friedman acid. The polarity (dipole moment) increases with the degree of metabolic transformations. For all the metabolites indicated, the HOMO form P = O bonds, while the LUMO are involved in intramolecular charge transfer with participation of both C–Cl groups.

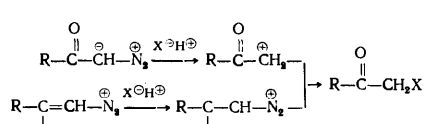
Comparison of the structures of the $S_n^*$ and $T_n^*$ excited levels of the cyclophosphamide metabolites and DNA bases showed that only Friedman acid has an arrangement of levels which ensures a satisfactory interaction with DNA. This conclusion agrees with data showing that Friedman acid has the most pronounced alkylating properties among all the cyclophosphamide metabolites and is at the same time capable of alkylating only nucleic acids but not enzymes. The ineffectiveness of the direct application of Friedman acid as a medicinal drug can be accounted for, according to the author,[45] by the poor transport properties of this compound in view of its high polarity.

The characteristics of the electronic structures of cytostatic agents comprising a series of phosphoric acid triamides have also been discussed.[46]

Electronic characteristics calculated by the CNDO/2 method and the antitumour activities of *p*-substituted diazoacetophenones.[4]

| R | $E_{HOMO}$ | $E_{LUMO}$ | Atomic charge, e | | Free valence index | Hammett constant σ | Inhibition of tumour growth, % | |
|---|---|---|---|---|---|---|---|---|
| | | | O | C | | | ARE | S-180 |
| $OCH_3$ | −10.959 | 1.916 | −0.375 | −0.186 | 0.122 | −0.27 | 79 | 70 |
| H | −11.013 | 1.896 | −0.372 | −0.172 | 0.114 | 0.00 | 64 | 63 |
| F | −11.144 | 1.441 | −0.343 | −0.162 | 0.066 | 0.06 | 30 | 44 |
| $NO_2$ | −11.697 | 0.959 | −0.324 | −0.158 | 0.050 | 0.78 | 25 | 32 |

A scheme for the interaction of alkylating preparations in the class of diazoketones with the acid groups of biomacromolecules has been analysed by means of the CNDO/2 method:[4]



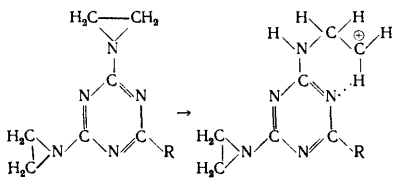
Calculation of the energies of the frontal molecular orbitals, free valence indices, and negative charges on the oxygen atom and the methylidyne carbon atom established a correlation between these parameters, the Hammett constants, and the antitumour activity of diazoketones (see Table).

Preparations containing the ethyleneimine group occupy an important place among alkylating ATC. The activation of such compounds reduces to the opening of the ring at the N–C bond in the protonated ethyleneimine and the formation of the carbonium ion $X-NH-CH_2-CH_2^+$.

Complete structural data about the disposition of all the atoms in ethyleneimine have been obtained by a non-empirical calculation in terms of the 4-21 HF basis set using gradient optimisation of the geometry.[47] The nitrogen atom is $sp^3$-hybridised and a value of 13.9 kcal mol$^{-1}$ was obtained for the barrier to inversion (the experimental values are in the range 11.6–19.1 kcal mol$^{-1}$). The structures and thermodynamic functions of the monohydrate complexes of ethyleneimine have been calculated.[48] The energy of the electrostatic interaction for the complex with the N–H...O(I) bond, with a $H_2O$ molecule acting as the $H^+$ acceptor, is −7.3 kcal mol$^{-1}$, while for the complex with the N...H–O(II) bond, with water as the $H^+$ donor, it amounts to −7.1 kcal mol$^{-1}$. The theoretical values of the free energies $F$ and the equilibrium constants proved to be −0.05 kcal mol$^{-1}$ and 1.093 for (I) and 1.42 kcal mol$^{-1}$ and 0.092 for (II). Thus the hydration of ethyleneimine at the N–H bond is more stable.

MINDO/3 calculation for the mechanism of the opening of the ring of protonated ethyleneimine showed[49] that the direct conversion into the carbonium ion requires an appreciable activation energy (45 kcal mol$^{-1}$). When an external nucleophile is involved ($Cl^-$ was used in the above study[49]), the reaction barrier is lowered to 25 kcal mol$^{-1}$. Thus ring opening without appreciable external influences is extremely difficult. The one-stage nucleophilic ring opening process via the $S_N2$ mechanism is energetically the most favourable.

Preparations of the class of substituted ethyleneiminotriazines have been synthesised:[50]



The authors postulated the formation of a stabilised intermediate form of the carbonium ion—a cyclic intermediate. The energy $E_Q = Q_C Q_N r_{CN}^{-1}$ of the electrostatic interaction of the terminal carbon atom of the carbonium ion and the nitrogen atom in the triazine ring was adopted as a characteristic of the stability of the above products. The atomic charges in the intermediate were calculated by the CNDO/2 method. Comparison of $E_Q$ and the antitumour effect for a series of five preparations showed that the effectiveness of the preparation increases with increasing stability of the intermediate (Fig. 2). The authors suggested that this effect can be accounted for by the similarity of the structures of the cyclic intermediate and the limiting transition state in the nucleophilic attack on the molecule to be alkylated.

Certain principles of the chemical modification of the alkylating ATC have been examined.[51] Electrophiles are consumed in the organism both via non-specific reactions involving nucleophilic centres in various chemical compounds and via specific reactions with the DNA bases in tumour cells. The second channel, which is the target of chemotherapy, is much less probable than the first. An increase of the relative number of specific reactions with target molecules can be achieved, according to the authors,[51] by ensuring the preferential occurrence of the alkylation reactions via the $S_N2$ mechanism as a result of the intramolecular stabilisation of carbonium ions. We may note that in the general case the degree of stabilisation of such a heterocyclic intermediate increases with increase in the nucleophilicity of the heteroatom X in the sequence O < N < P < S and with decreased ring strain energy. As an example of the use of this concept, the mechanisms of the action of ATC based on phosphamide and diazoketones were examined.

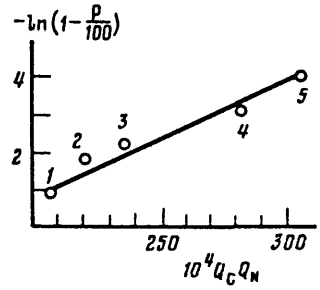
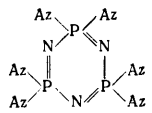



Figure 2. Dependence of the antitumour effect $P$ of ethyleneiminotriazines on $10^4 Q_C Q_N$ (correlation coefficient 0.98): 1) $C_2H_5$; 2) $OC_2H_5$; 3) $OCH_3$; 4) OPh; 5) $OCH_2Ph$.[50]

The conformational and electronic properties of the ATC in the group of aziridinocyclophosphazans have been investigated.[52–54] Using a computer, the disposition of the ethyleneimine groups in different crystalline forms of the preparations was analysed graphically.[53] The differences between the structures of the preparations associated with the influence of the substituents and solvent molecules in the crystal lattice reduce to differences in the orientations of the aziridine rings:



Quantum-chemical calculations (CNDO/2) of the barrier of the rotation of the aziridine group demonstrated the existence of three energy minima, corresponding to crystalline modifications of the preparations. For the three preparations, $N_3P_3Az_6$, $(NPAz_2)(NSOAz)$, and $SPAz_3$ (thiophosphamide), where $Az = -NCH_2CH_2$, the atomic charges and Wiberg indices were calculated by the CNDO/2 method.[54] All the experimentally detected crystalline conformations of these ATC were examined. The reactivities were analysed from the standpoint of the possible activity of these preparations as alkylating or intercalating agents for DNA.

The alkylation of DNA by the carbonium ions derived from the ethyleneimines was examined as a process involving the coordination of Lewis acids and bases. Analysis of the atomic charges led to the conclusion that the antitumour activity is determined by the acidity of the P atom. The phosphorus atoms in the preparations $N_3P_3Az_6$ and $(NPAz_2)(NSOAz)$, which are more ative than $SPAz_3$, are correspondingly more "acid". On the other hand, comparison of the charges in other ATC—*cis*-$Pt(NH_3)_2Cl_2$ and its inactive analogue $Pt(AzH)_2Cl_2$—showed that the Pt atom has a markedly "acid" character. The total charge on the Pt atom in the first Pt salt was 0.998 (calculation by the Xα method[55]). As a result of this, the coordination of the ethyleneimine groups to the Pt atom in $Pt(AzH)_2Cl_2$ is via the unshared electron pairs of the nitrogen and the formation of the corresponding carbonium ion is difficult. According to the authors, this in fact

accounts for the low antitumour activity of $Pt(AzH)_2Cl_2$. It was concluded that the manifestation of a high antitumour activity by an ethyleneimine-containing compound requires that the atoms linked to ethyleneimine should have the optimum positive charge (−0.35e). We may note that the specific value of the optimum charge is consistent with the calculation by the CNDO/2 method.

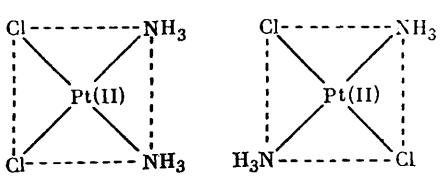
Quantum-chemical calculation (CNDO/2) of the electronic structure and stabilities of new classes of preparations of the type $[NP(CH_3)_2]_{3-x}.(NCNCH_3)_x$ and $(NPCH_3)_{3-x}.(NCNCH_3)_x$ ($x$ = 0, 1, 2, 3) [52] made it possible to predict that the compounds with $x$ = 1 and 2 may exhibit more effective antitumour properties than the familiar preparations $N_3P_3Az_6$. The authors' conclusions[52] have been confirmed by biological tests.

Thus the available data permit the following conclusions about the electronic mechanisms of the alkylation reactions: (1) in a specific calculation of the reaction mechanisms, it is apparently essential to take into account charge transfer states; (2) in ethyleneimine-containing ATC, the atoms close to this group play an important role. In particular, since the opening of the aziridine ring requires the involvement of an external nucleophile,[49] the nucleophilic centres of the molecule itself can in our view function as such a nucleophile. These centres are capable of subsequent participation in the intramolecular cyclisation of the carbonium ion, stabilising it, which can apparently promote the selective interaction of this carbonium ion with the nucleophilic centres of DNA.[50,51]

## 2. The Formation of Complexes by Antitumour Compounds

According to Emanuel's classification, preparations the mechanism of whose therapeutic action is associated with the formation of molecular complexes with biomacromolecules should be classified as complex-forming ATC. At the present time this class includes metal complexes and salts (in the first place platinum complexes and gallium nitrate) and intercalating agents. The principal target of these preparations is DNA.

The most familiar of the platinum-containing preparations is "*cis*-chlorodiaminoplatinum". The ATC based on paltinum(II) form "intercalating" intermolecular and intramolecular cross-links with DNA.[56] The cross-links are formed mainly via the 6-amino-groups of the adenine residues of the opposite chains of DNA and the N(7) atoms of the guanine residues in the G–G pairs. The electronic structure and the parameters of the reactivity of the metal salts have been calculated.[55,57–64]




*cis*-Pt(II) *trans*-Pt(II)

The electronic structures of the platinum complexes $PtCl_4^{2-}$, $Pt(NH_3)_4^{2+}$, *cis*-$Pt(NH_3)_2Cl_2$, *trans*-$Pt(NH_3)_2Cl_2$, and $Pt(CN)_4^{2-}$ have been calculated in terms of the approximation of the extended Hückel method (EHM) with adjustment for self-consistency on the basis of the density matrix in terms of the relativistic basis set ($5s_{1/2}$, $5p_{1/2}$, $5p_{3/2}$, $5d_{5/2}$, $6s_{1/2}$, $6p_{1/2}$, $6p_{3/2}$) and the Pt(II) AO.[57] Quasi-relativistic corrections were taken into account in terms of the "frozen" spin approximation. In constructing the Hamiltonian, corrections were introduced to take into account the external stabilising potential. The main contribution to the coefficients of the HOMO of *cis*-Pt(II) comes from the ligands, but there is an admixture of the 5*d* and 6*s* AO of platinum. On the other hand, in the case of *trans*-Pt(II) 6*p* and 5*p* AO of platinum contribute an admixture to the HOMO. The difference between the antitumour activities of these preparations (*trans*-Pt is inactive) may be associated with this factor according to the authors. Calculations were made for the complexes of *cis*-Pt(II) with guanine and the guanine-cytosine pair coordinated to the O[C(6)] and N(7) atoms. The possible mechanism of the molecular action of *cis*-Pt(II) involves the dehydrogenation of the N(1) atom of guanine, although a weakened N(1)–H bond has not been observed in the complexes investigated.

Calculations for *cis*- and *trans*-Pt(II) by the SCF-Xα method, which is widely used for calculations on organometallic compounds, did not reveal any significant differences between their electronic structures.[55] It has been suggested that the differences between the biological activities of these isomers are associated with steric and not electronic factors.

The characteristics of the structure of the hydrate complexes of dichloroaminoplatinum have been investigated[61] by the LCAO-MO method in the Mulliken–Wolfsberg–Helmholz version with adjustment for self-consistency with respect to the charges. In the complexes $[Pt(NH_3)_2XY]^{n+}$ (X, Y = Cl, $H_2O$; $n$ = 0, 1, 2), the chemical bond with the ligand is formed via the 6*s* and 5*d* AO of platinum. The aquo-complexes $[Pt(NH_3)_2(H_2O)_2]^{2+}$, formed in the course of hydrolysis, possess effective electron-accepting properties and should readily interact with the nucleophilic sections of DNA. According to the calculation, *trans*-Pt(II) is more acid and is more readily hydrolysed than the *cis*-isomer. This result agrees with experimental data. It has been concluded that there is a possibility of the rapid deactivation of *trans*-Pt(II) in the organism as a result of hydrolysis, which the authors used in face to explain the absence of an antitumour effect by this compound. In our view, this explanation is better founded and more likely than the hypotheses put forward by Barber et al.[57] and Boudreaux and Carsey.[57]

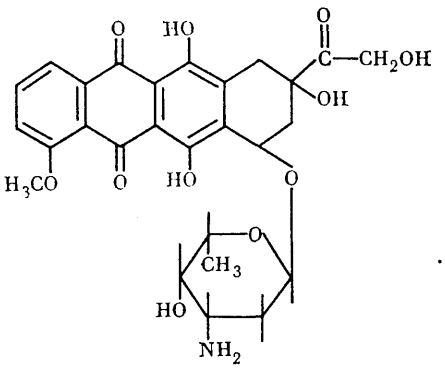
The structure–activity relations for a series of 26 dichloroaminoplatinum(II) complexes have been investigated.[62] The following RI were calculated by the INDO method (with special parametrisation for calculations on metals[63]): the frontal densities $f^N$, the binding energies of the complexes $W_b$, the molecular volume $V_M$, the electrostatic potential and the electric field strength $E$, and the energy $V_2$ of the polarisation interaction of the complex with a single charge. The RI were compared with the logarithms of the doses inducing the death of 50% of the animals ($LD_{50}$), 90% inhibition of tumours ($TD_{90}$), and their ratios. The two-parameter linear regression with the highest statistical reliability has the form

$$\lg(LD_{50}) = 0.0021\,(\pm 0.0008)\,W_b + 4.06\,(\pm 1.4)\,V_2 + 8.34\,(\pm 1.2),$$
$$r = 0.820,\ S = 0.37,\ F(2.23) = 23.65,$$

where $r$ is the multiple correlation coefficient, $S$ the standard deviation of the regression line, and $F(2.23)$ the value of the $F$-statistic. A relation with a correlation coefficient $r$ = 0.817 between $\lg(LD_{50})$, on the one hand, and $V_M$ and $V_2$ on the other, was also obtained. Thus the toxicity of the preparations is higher the greater the polarisability of the complex, the less stable the molecule, and the greater its molecular volume. However $V_M$ and $E_b$ have a high mutual correlation coefficient and the authors were unable to discover which of these quantities must be excluded from consideration. The quantity $\lg(TD_{90})$ is less well correlated with electronic parameters. The regression equation with the best correlation coefficient $r$ = 0.626 includes $E^2$ and $f^N$.

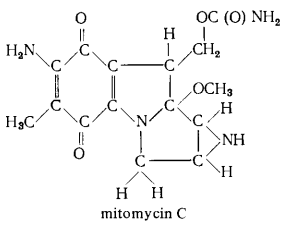
Since the electric field vector $E$ is directed at right angles to the plane of the intercalation complex, the correlation between $\lg(TD_{90})$ and $E^2$ casts doubt on the intercalation mechanism of the action of *cis*-Pt(II).

The anthracycline antibiotics belong to the class of ATC capable of reacting with DNA via intercalation. The conformational analysis of anthracycline antibiotics has been carried out:[65-67]



Attention has been concentrated on the determination of the equilibrium orientations of the sugar residue and the hydroxy-groups relative to the anthracycline chromophore. Calculation for adriamycin by the force field method (with and without allowance for the influence of the aqueous environment) indicates the formation of intramolecular hydrogen bonds between the hydroxy- and keto-groups of the chromophore.[66] Three equilibrium positions have been found for the carbohydrate fragment. The conformation which corresponds to that observed in the crystal has an energy higher by 3 kcal $mol^{-1}$ than that of the lowest-energy conformation. The absolute energy minimum obtains for the conformation in which there is a hydrogen bond between the hydroxy-group in the 6-position and the O atoms of the sugar residue. The third equilbrium conformation, which corresponds to the almost parallel disposition of the carbohydrate residue relative to anthraquinone, is destabilised to the extent of 9.5 kcal $mol^{-1}$ relative to the most stable conformation. The influence of the solvent on the relative stabilities of the conformers is insignificant. It follows from the proposed model that, for the equilibrium conformation found, there is a possibility of an additional stabilising interaction of the protonated $NH_3^+$ group of the sugar ring of the anthracycline and the phosphate groups of the DNA double helix. The conformations of the form of the antibiotic with a protonated sugar residue are identical to those in the neutral state.[66]

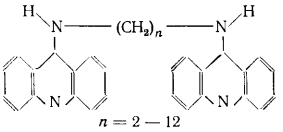
The characteristic features of the intercalation by the antitumour antibioltic mitomycin C have been investigated:[68]



mitomycin C

The interactions of the antibiotic with the model guanidine-(3',5')-cytidine dinucleotide and all possible pairs of nucleic acid bases were examined. The intermolecular interaction energy was calculated on the basis of two additive schemes—purely empirical and imitating the results of non-empirical calculations. The orientation of the antibiotic was varied within wide limits. All the optimum positions found are located at the site of the major groove of DNA. The non-planar part of the antibiotic molecule interferes with the complete intercalation of the planar quinonoid part. The intercalation on the side of the minor groove gives rise to a relatively unstable complex as a consequence of the weak overlap of the aromatic rings. The two methods of calculation yielded somewhat contradictory data concerning the optimum orientation of the axis of the quinonoid fragment relative to the dinucleotide. An increased specificity in the intercalation of any one pair of DNA bases by the antibiotic was not found.

The relation between the antitumour activity and the characteristic features of the intercalation has been investigated for a series of diacridines.[69] The RI for the neutral forms of 27 compounds were calculated by the CNDO/3R method.



Three molecular conformations were examined: (1) the planar conformation with a symmetry axis; (2) the planar conformation with a symmetry centre; (3) the non-planar conformation with a parallel arrangement of acridine rings. These conformations correspond to different models of the intercalation by one or simultaneously two acridine rings in DNA. QSAC have been investigated for the indices of the inhibition of the *in vitro* growth of P388 cells ($I_{50}$) and the toxicity ($LD_{10}$) in mice. It follows from the analysis of the QSAC that the molecular size is correlated with $\lg(I_{50})$ and $\lg(LD_{10})$. The length of the alkyl chain between the rings does not influence the biological indices. The stability of the bonds involving the nitrogen atom in the acridine ring has a positive correlation coefficients with $\lg(LD_{10})$. For the planar forms, the energy of the N–H bond has a negative correlation coefficient with toxicity and a positive correlation coefficient with the effectiveness of the inhibition of the P388 leukaemia. According to the authors,[69] the latter factor shows that the biological activity is associated with the freedom of the rotation of the planar part of the molecule about the C–N bond relative to the intercalated acridine ring.

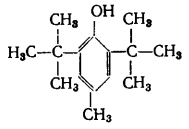
Together with the intercalation mechanism of the cytotoxic activity, alternative mechanisms of the action of a series of antibiotics are now being considered. Thus the biological effect of the anthracycline antibiotics may be based on the formation of free-radical intermediates of the semiquinone type and active forms of reduced oxygen.[70] The molecular mechanisms of the action of mitomycin C includes the formation of reactive polyfunctional intermediates—carbonium ions and semiquinone free radicals—which leads to alkylation and cross-links between the complementary chains of DNA.[71]

### 3. Compounds whose Activity Has a Free Radical Mechanism

It has now been established that many metabolic and pathological processes in the cell proceed via a free-radical mechanism.[1,70-72] This applies in the first place to $e^-$ transfer reactions in the enzymic oxidation and reduction of substrates of different nature and to the lipid peroxide oxidation reactions. The products of the metabolism of many BAC are free-radical in nature (an unpaired electron is present). The intensification of the formation of free radicals in tumours is characteristic of specific stages in tumour development and this is why the inhibitors of free-radical processes can inhibit the growth of malignant formations.[1] Thus

compounds whose antitumour activity is associated with the inhibition of free-radical processes in tumour cells or is determined by free-radical products of their metabolism should be classified as ATC whose activity has a free-radical mechanism.

Compounds belonging to the group of sterically hindered phenols are included among the bioantioxidants used to fight tumour processes. The preparation dibunol (2,6-di-t-butyl-4-methylphenol) is used as an ATC in therapeutic practice.



dibunol

The conformational properties and reactivity of dibunol and its metabolites (aryloxy-radical, 2,6-di-t-butyl-4-hydroxymethylphenol, and 2,6-di-t-butyl-4-carboxyphenol) have been investigated by the MINDO/3 and INDO methods.[36] A partial optimisation of the geometry has been carried out for two conformations of dibunol, which correspond to two forms of associated species with solvent molecules. In one of them (I), the proton of the OH group lies in the plane of the benzene ring, while in the other (II) the OH group is rotated by 90° relative to the plane of the ring. According to the calculations, the conformation (II) is more stable than the conformation (I) by 1.2 kcal $mol^{-1}$. For both dibunol and for its aryloxy-radical, the C–O bond lies outside the plane of the ring. It follows from the MEP maps which have been constructed (Fig.3) that there is a deeper potential minimum in the conformation (II) (−95.2 kcal $mol^{-1}$) than in the conformation (I) (−88.4 kcal $mol^{-1}$). In the conformation (I) the proton and the unshared electron pair of the OH group are more shielded by the t-butyl substituents than in the conformation (II). The hydrophilic properties of dibunol and its metabolites have also been estimated.[36] The energy of the electrostatic interaction of the phenols with a water molecule averaged on the van der Waals surface was adopted as a measure of hydrophilicity. The conformation (II) is stabilised to a greater extent by the interaction with water than the conformation (I). The hydrophilicity indices are in satisfactory qualitative agreement with the experimental values of the lipophilicity parameter $\pi$ for the phenols considered.

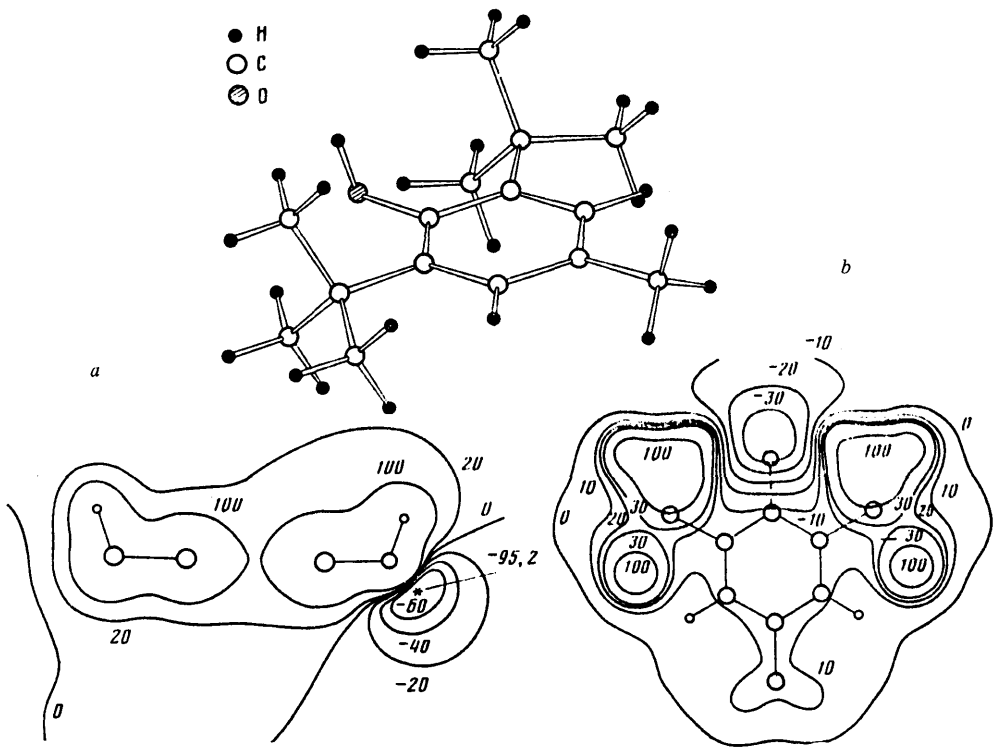
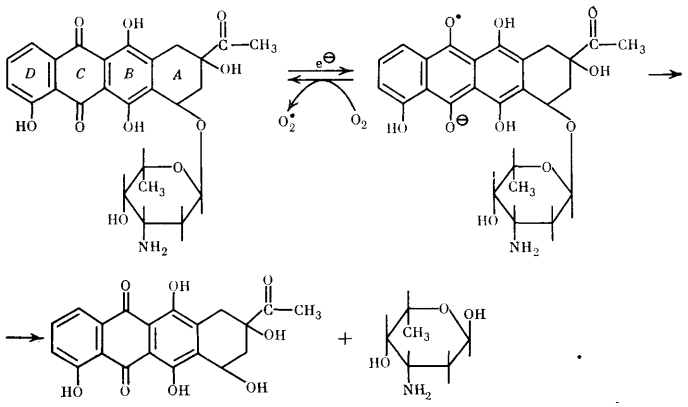


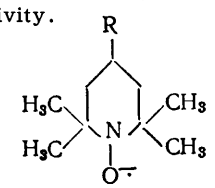

**Figure 3.** Projection of the three-dimensional structure of dibunol and the isopotential MEP maps (kcal $mol^{-1}$): *a*) in the plane of the OH group; *b*) in the plane located 1.5 Å above that of the benzene ring.[36]

The antitumour anthracycline antibiotics (AAA) may be included among the ATC whose activity has a free-radical mechanism. They act on various cell organelles—they intercalate DNA, are bound to membranes, and form radicals of the semiquinone type in enzymic reduction. The free semiquinone radicals of AAA are capable to exhibiting biological effects of two types: (1) they can generate the toxic superoxide radical-anions $O_2^{\cdot-}$ as a result of oxidation by molecular oxygen;[70,72] (2) they can bind to DNA—tentatively via an oxidative alkylation mechanism.[73]



Studies on the conformational properties of AAA and the characteristic features of the intercalation of DNA have already been considered.[65-67] The oxidation-reduction properties and reactivities of four antibiotics (rubomycin, carminomycin, adriamycin, and aclacinomycin A) and their free radicals have been investigated by the quantum-chemical INDO method and by EPR.[74,75] In order to take into account the influence of the solvent, tne hydrate complexes of the antibiotics were examined. It was shown that in the presence of $H_2O$ molecules, the hydroxy- and keto-groups of the anthraquinone chromophore can form intermolecular hydrogen bonds with the solvent more readily than the intramolecular hydrogen bond with one another. According to the calculation, the principal splittings in the EPR spectrum of the radical-anion are associated with the protons of the *A* ring. Wiberg analysis of bond order showed that the glycosidic C–O bond between the *A* ring and the sugar residue is weakened in the radical-anions. In view of the weakening of this bond, one can postulate the possibility of the spontaneous abstraction of the sugar residue. This has been confirmed experimentally by observing the solubility of AAA in their reduction in an aqueous medium.[74] The appearance of the EPR signal of the radical-anions is accompanied by the formation of a deposit in the reaction mixture which may be associated with the elimination of the carbohydrate fragment and the formation of the antibiotic aglycones, which are sparingly soluble in water. Comparison of the energies of the frontal MO, characterising the redox properties of the AAA, with the toxic doses $LD_{50}$ did not reveal a relation between these characteristics. Thus the differences between the toxicities of the antibiotics could not be linked by a simple relation to the capacity of their radical-anions for oxidation by molecular oxygen.

The stable nitroxy-radicals are used to modify ATC, for example anthracycline antibiotics, and themselves exhibit a weak antitumour activity.



Calculations have been made[76,77] by the INDO method of the electronic structures of 7 derivatives of the piperidin-*N*-yloxy-radicals and their reduced forms—anions and hydroxylamines. For the series of radicals investigated, a weak dependence of the electronic characteristics of the $N-O^{\cdot-}$ fragment on the nature of the substituent was observed, which has been attributed to the appreciable localisation of the MO of the oxy-group and of the substituent in the 4-position. For all the species examined, the electron in the anion is localised at the oxy-group. The redox properties of the radicals were estimated from the differences between the total energies of the anions and radicals and from the energy $\varepsilon_{HOMO}$ of the anions and hydroxylamines. It was established that only the HOMO energies describe correctly the experimental reduction potentials. In order to estimate the transport properties of the radicals, the average electrostatic energies $W_h(R^{\cdot-})$ of the interaction with a $H_2O$ molecule on the van der Waals surface of the nitroxy-radicals[77] were calculated analogously.[36] The electronic parameters of the compounds investigated were compared with data for their acute toxicity and antitumour activity. The inhibition coefficients $\kappa$, characterising the antitumour activity have virtually identical values ($\kappa = 1.0-1.1$) for the radicals studied. Presumably $\kappa$ is determined by the electronic parameters, which are constant in this series.

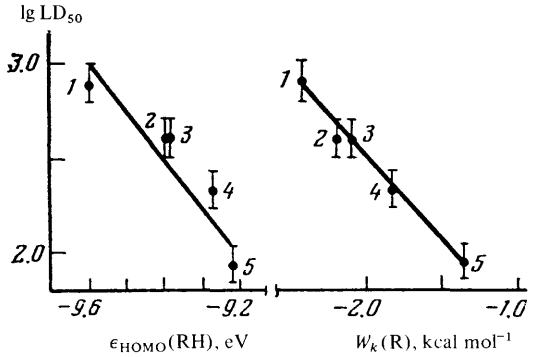
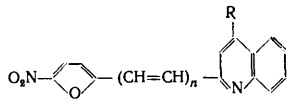



**Figure 4.** Dependence of the toxicity $LD_{50}$ of piperidin-*N*-yloxy-radicals on the hydration energy $W_h(R)$ (correlation coefficient 0.99) and the energy $\varepsilon_{HOMO}(RH)$ (correlation coefficient 0.94): 1) =O; 2) OH; 3) NHC(O)$\overline{NCH_2CH_2}$; 4) OC(O)NHPh; 5) $CH_2NH_2$.[77]

The results of the calculations support the current hypothesis that the antitumour activity of the nitroxy-radicals is associated with their antiradical properties,[1] since the spin densities on the $N-O^{\cdot-}$ fragment, which to a large extent determine its reactivity, remains constant in the series considered. Three statistically significant relations of the type of the Hansch equation between $LD_{50}$, on the one hand, and $W_h(R^{\cdot-})$, $\varepsilon_{HOMO}(R^-)$, and $\varepsilon_{HOMO}(RH)$, on the other, have been obtained.[77] According to these correlations, an increase in the hydration energy and the enhancement of the electron-accepting properties of the nitroxy-radical lower its toxicity (Fig. 4). In the organism, the radicals are rapidly reduced and exist mainly in the form of hydroxylamines. It has been concluded that the oxidation reactions of their reduced forms, leading to the formation of toxic products of the reduction of molecular oxygen, may be responsible for

the toxicity of these species. In view of the dependence of $LD_{50}$ on $W_h(R^-)$, one can then assume that biological membranes owe the sites at which chemical reactions responsible for the toxic effect take place.

A broad spectrum of the antitumour activity (in experimental animals) is characteristic of vinylquinoline derivatives of 5-nitrofuran.

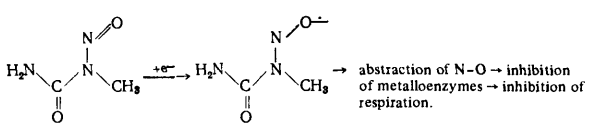


$n = 1,2$

The molecules of these compounds contain two groups which are potentially capable of exhibiting an antitumour effect—the nitro-group and the quinoline ring. It is so far not clear which of these groups is responsible for the antitumour activity. It is known that other types of biological activity of nitrofuran derivatives (antibacterial activity, the formation of nitrosyl complexes, and the generation of superoxide radicals-anions $O_2^-$) are associated with the reduction of the nitro-group. Quantum-chemical calculations (INDO, MINDO/3) of the electronic, conformational, and spectroscopic properties of a wide range of nitrofuran derivatives have been carried out[78] and it has been shown that the nitro-group determines the pronounced electron-accepting properties of 5-nitrofuran derivatives. The unpaired electron in the radical-anions of the vinylquinoline derivatives is localised mainly at the nitro-group (according to the calculation with allowance for the specific solvation of the $NO_2$ group). The electron-accepting properties of compounds of the vinylquinoline series are close to those of other derivatives of 5-nitrofuran with a high biological activity. A correlation between the electronic constants of the substituents and the antitumour activities of nitrofurans has also been observed.[79]

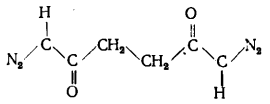
Free-radical mechanisms of the biological activity have also been proposed for two ATC derived from nitrosourea and 1,2-bisdiazoacetylethane (diazan), which have been traditionally regarded as alkylating preparations.[1,3]

The study of the electronic structures of the radical-ions of nitrosoalkylureas made it possible to predict initially[80] and then confirm experimentally the existence of a new pathway leading to the metabolic transformations of the nitrosourea, which involves the formation of nitrosyl complexes by haem-containing enzymes:[83]




The electronic parameters of the neutral state and the radical-anions of nitrosourea, in nitrosomethylurea, nitrosoethylurea, and their decomposition products (an aminoaldehyde and a nitrosamine) have been calculated by the INDO method[80,81] and by the MNDO and *ab initio* methods.[82] The electron-accepting properties and the ionisation potentials increase as follows in the series of alkyl substituents: $H < CH_3 < C_2H_5$. Both on ionisation and on capture of $e^-$, the greatest change in the charge takes place on the nitroso-group. The spin density in the radical-ions is also localised mainly on the nitroso-group. The mechanism of the decomposition of the radical-anions has been proposed on the basis of the analysis of the Wiberg bond orders.[80,81] When $e^-$ is transferred to alkylnitrosourea, the N–N bond order is appreciably weakened (by 0.2 e.s.u.), i.e. elimination of the NO group becomes possible either spontaneously or via the formation of a complex with an iron atom (in model systems). In the enzymic reduction of the preparation, the formation of a complex with the $Fe^{2+}$ atom in the active centre is apparently followed by the synchronous transfer of $e^-$ to the preparation, a weakening of the N–N bond, and the elimination of the NO group. The formation of nitrosyl complexes leads in the first place to the inhibition of the respiratory chain, but it may be that the antitumour effect is also associated with this factor. The finding that the greatest weakening of the N–N bond is characteristic of methylnitrosourea,[80] which exhibits the greatest antitumour activity among the above three preparations, merits attention.

Quantum-chemical calculations for diazan as an ATC have been carried out.[84,85] The study of Kartsev et al.[84] was devoted to the X-ray diffraction and quantum-chemical (CNDO/2) investigation of the structure of the diazan molecule:



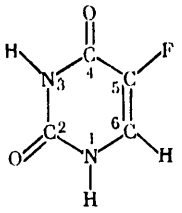
diazan

Luzhkov et al.[85] analysed the reactivity of diazan from the standpoint of its free-radical reactions. For this purpose, a study was made by the INDO and EPR methods of model oxidation-reduction reactions of these preparations. The EPR signal of free radicals of the type $X-CH_2-CH_2^{\cdot}$ (X represents the diazoketone fragment), which are capable of adding to biomolecules, was recorded in aqueous solutions of diazan in the presence of hexacyanoferrate(III), a powerful acceptor, on irradiation with light ($\lambda$ = 340–380 nm). The equilibrium conformation of diazan was determined by means of a quantum-chemical calculation and the changes in its electronic structure in $e^-$ transfer reactions were calculated. Both electron capture and electron elimination entails a rearrangement of the system of conjugated $\pi$ electrons in one of the two diazoketone fragments. The maximum spin density is localised on the oxygen atom in the radical-cation. The elimination of an electron is accompanied by the destabilisation of the structure of the diazoketone fragment. According to the calculations, the diazan molecule is a weak electron donor with $IP$ = 9.1 eV. However, when the diazo-group is displaced from the plane of the diazoketone, the ionisation potential is reduced by 0.5 eV. Presumably this conformation corresponds to the transition state in the enzymic oxidation of the molecule. Thus, as the molecular level, the activity of diazan can be attributed to its enzymic oxidation and to the alkylating activity of the $X-CH_2-CH_2^{\cdot}$ radical formed on decomposition of the diazan radical-cation.

## 4. Antimetabolites and Certain Other Types of Preparations

An important class of antitumour preparations comprises antimetabolites. Their activity is based on structural similarity to vitally important products of cell metabolism—nucleic acids, aminoacids, and enzyme substrates. By entering into biochemical reactions instead of the true metabolites, antimetabolites suppress the vital activity of the cell. There exist antimetabolites capable of acting selectively on actively dividing tumour cells.

Calculations have been made on 5-fluorouracil (5FU)—a preparation widely used in clinical practice.[86-89]



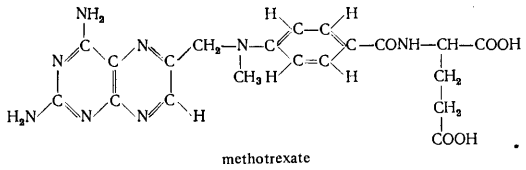
5-fluorouracil

5FU is a powerful inhibitor of the enzyme thymidylate synthetase, which is involved in an important stage in the synthesis of DNA—the methylation of uridine monophosphate to thymidine monophosphate. The differences between the reactivities of 5FU and pyrimidine bases have been deduced with the aid of quantum-chemical calculations. The relative stabilities of six lactim–lactam 5FU tautomers have been examined[89] with total optimisation of the geometry in terms of the 3-21 basis set of split Gaussian functions. The lactam form is the most stable both for the isolated tautomers and when account is taken of the interaction with water.

The reactions of uracil, thymine, 5FU, and 5-trifluoromethyluracil (which also exhibits an antitumour activity) with $O_3^{2-}$, adopted as a model of their interactions with thymidylate-synthetase, has been investigated.[87] As for the enzyme, a two-stage mechanism of the interaction was considered: (1) nucleophilic attack on the C(6) atom; (2) electrophilic attack on the C(5) atom in the 6-*S*-anion formed in the first stage. The quantum-chemical calculation was performed by the non-empirical method in terms of a basis set of floating spherical Gaussian functions and with subdivision of the molecule into fragments. It follows from the populations and bond orders involving the HOMO and LUMO that the specificity of the nucleophilic attack on C(6) and electrophilic attack on C(5) of the anion is determined by electronic factors. Both reactions take place with participation of $\pi$ electrons. The F atom has a complex influence on the rate of the overall reaction. As a consequence of the resonance interaction, the electron density on the C(6) atom in 5FU is higher than in uracil, which should retard stage 1. On the other hand, it follows from the analysis of the electron population and the additionally calculated protonation energies that the influence of the F atom in the anion leads to an increase of the basicity of the O[C(2)] atom. The energies of the protonation of O[C(2)] decrease in the same sequence as the overall rate constants for the reactions with bisulphite: 5FU > uracil > thymine. This correlation agrees with indirect experimental data indicating the importance of the mechanism of the protonation reaction and suggests that the protonation of O[C(2)] determines the rate of the overall reaction. It has thus been explained why 5FU interacts with the enzyme more effectively than uracil. Data have also been published[86,88] concerning the interpretation of the photoelectron spectra of 5FU and pyrimidine bases as well as the energies of their complexes.

The correlations of quantum-chemical RI with the ability to inhibit dihydrofolate reductase (DHFR) have also been investigated for several classes of compounds.[90-95] DHFR is involved in the conversion of folic acid into tetrahydrofolic acid, which is essential for the synthesis of nucleic acids. Antimetabolites inhibiting DHFR inhibit the growth of tumours. In this connection new effective inhibitors of this enzyme are being sought. Calculations have been made for compounds of the class of quinazolines (series of 25 [90] and 48 [91] preparations), pteridines and triazines[97] (17 compounds), and diaminobenzylpyrimidines[93] (23 compounds). RI analogous to those for which calculations had been made by Abdul-Ahad and Webb[62] were studied in other investigations.[90-92] The potentials of interactions with trial species ($H^+$, $O^-$, $CH_3^+$) were calculated for diaminobenzylpyrimidines and six new descriptors were proposed on the basis of a description of the effects of interaction with the active centre. Despite the fact that statistically reliable regressions have been obtained between certain RI and the DHFR inhibition rate constants, the final conclusion concerning the mechanism of the interaction of the preparations with the enzyme was not reached. Nor is it stated whether the relations established were used to synthesise new ATC. The importance of the electronic parameters of the pyrimidine ring for quinazolines was noted. In particular, the localisation of $\pi$ electrons in the pyrimidine ring is unfavourable for the manifestation of activity.[91] In the case of triazines the regressions for enzymes derived from normal and tumour tissues are very similar.[92] It was concluded that such QSAC are unsuitable for use in the search for substances with an enhanced specificity towards tumours.

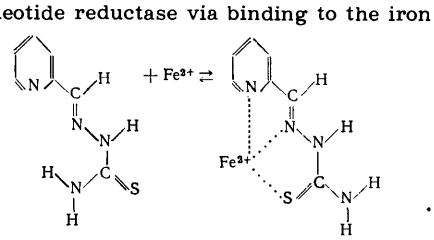
A non-empirical calculation of the energy of the binding of methotrexate, a preparation used in chemical practice, to DHFR has been carried out:[96]



methotrexate

The coordinates of the atoms of the enzyme–substrate complex were taken from X-ray diffraction data. The atoms of the active centre in DHFR were modelled by point charges, which made it possible to take into account their influence without calculating the integrals for the electron–electron interaction. It was assumed that the environment of the substrate includes 17 aminoacid residues. The methotrexate molecule was divided into six fragments because of the impossibility of carrying out the calculation for the molecule as a whole and the binding energy was calculated on the basis of an additive scheme. The value obtained (−62.69 kJ $mol^{-1}$) agrees with experimental estimates within the limits of 10 kJ $mol^{-1}$. According to the authors, the procedure proposed for the calculation of the energy of binding to the active centre is fairly simple and can be used for the screening of preparations.

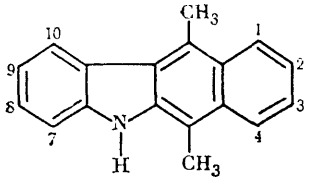
Semiempirical quantum-chemical calculations have been made[97-100] for yet another class of antitumour antimetabolites—derivatives of thiosemicarbazone (TSC). The mechanism of the action of these substances consists in the inhibition of ribonucleotide reductase via binding to the iron atom.



Calculation of the energies of the conformers of the pyridine derivative of TSC (PPP and PCILO methods with allowance for the Coulombic interaction with the solvent) showed that the given molecule has different equilibrium conformations in the free state and in the complex with $Fe^{2+}$.[100] The equilibrium configuration of the complex is identical with that

established crystallographically. The character of the binding of $Fe^{2+}$ and $Fe^{3+}$ ions to TSC derivatives has been investigated[97] by the extended Hückel method and from the electronic absorption spectra. There is a possibility of $Fe^{2+}$ forming an ionic complex with the neutral form and a covalent complex via the S atom with the forms of TSC deprotonated at one of the nitrogen atoms. Analysis of the absorption spectra of TSC and its homologues containing the methyl or morpholinyl group instead of one of its labile protons supports the operation of a covalent mechanism of the binding of $Fe^{2+}$ and of an ionic mechanism of the binding of $Fe^{3+}$. It follows from the calculations of the total energies that the $Fe^{2+}$ complexes with neutral molecules are more stable than those with the deprotonated forms. However, the binding of iron can reduce somewhat the $pK_a$ of the N–H group of the ligand. It follows from the EHM calculations for five pyrimidine and pyrazine derivatives that charge interactions play a decisive role for ionic binding, while the distribution of frontal densities is of decisive importance for covalent binding. Correlations between the RI of the anions of the isoquinoline derivatives of TSC (15 compounds) and their antitumour activities have been investigated.[98] On the basis of the model of the molecular activity employed, it was impossible to describe the changes in capacity to inhibit ribonucleotide reductase. Analysis of the distribution of the MO coefficients of TSC derivatives showed[99] that in the active preparations the HOMO corresponds to the unshared electron pair of the S atom, while in the inactive preparations it corresponds to the $\pi$ electrons of the S atom.

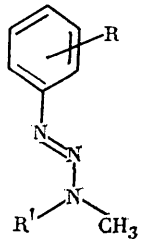
A quantum-chemical calculation (CNDO/2) for the antitumour antibiotics ellipticine, olivacine, and 2-methylellipticine has been carried out.[101] The stability of their oxidation products in the organism has been investigated. Hydroxylation proceeds most readily via the epoxide → diol (*trans*) → hydroxy-form pathway.




ellipticine

It has been shown that 9-hydroxy-isomer, which is the principal metabolite of these ATC, is less stable than the 7-, 8-, and 10-hydroxy-isomers. The antitumour activities of these compounds may be associated with the oxidation of the hydroxy-form to the quinone imine form. The ionisation potentials, calculated taking into account the solvation effects in terms of the approximation of virtual charges, did indeed show that the more active 9-hydroxyellipticine is oxidised more readily than hydroxyolivacine.

Correlations between electronic structure and antitumour activity have also been investigated for dimethyltriazene derivatives.[102–104] The molecular mechanism of the antitumour activity of these compounds is so far obscure. A series of RI have been calculated[102] for 15 derivatives of dimethylphenyltriazene.




The two-parameter QSAC obtained contain terms associated with the properties of the benzene ring, which may be due to the influence of this group on the transport of the preparation across membranes. Definite hypotheses concerning the mechanism of the biological activity could not be reached from the analysis of the terms of the regression equation referring to the triazene group Two types of QSAC have been established[104] for phenyltriazenes as a function of the type of tumour. A relation with the energy of the secondary protonation of the triazene group has been obtained for sarcoma-180, but no relation has been found between the activity in relation to leukaemia L1210 and the properties of this group. Such negative results may be accounted for by the fact that, according to Meyers,[105] phenyltriazenes may exhibit an immunostimulating activity rather than a cytotoxic activity.

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Quantum-chemical calculations in the field concerned with the synthesis of new medicinal drugs have their advantages and limitations. Modern quantum biochemistry with its great potential computational capacity can be regarded as a physicochemical approach close to the experimental one. Its objects are molecular models with a relatively small number of atoms. Quantum-chemical calculations for such models yield a general picture of the structure of electron shells and make it possible to estimate properties which are difficult to observe experimentally. Direct conclusions based on the results of calculations are concerned with the effect of BAC on biological objects at different molecular levels. It is apparently impossible to understand all the properties of the organism at the cellular and even supermolecular level on the basis of calculations for the most complex system. For example, quantum-chemical calculations are clearly inadequate for the description of the functioning of individual components of the ribosome. Quantum chemistry cannot and should not replace the experimental methods for the investigation of living organisms. Nevertheless, many events at the level of the cell and the organism ultimately reduce to processes at the molecular and electronic level. Szent-Gyorgyi stated that, whatever our approach to biology—from the side of matter or from the side of energy—we arrive at electrons in one way or another.[106] Quantum-chemical calculations are in fact most useful in the study of such phenomena.

From the investigations described above, it is evident that in recent years quantum chemists have obtained notable results in the study of the electronic structures and reactivities of the ATC and their metabolites, sections of DNA, and peptides which are vulnerable to the action of damaging factors. Interest has recently arisen in studies of the interaction of BAC with the active centres of enzymes. Such processes belong to the class which is difficult to investigate experimentally. It may be expected that quantum-chemical calculations will in fact provide in future a detailed molecular picture of enzyme processes on the basis of which it will be possible to select molecules with a potentially high specified activity, including antitumour activity.

Quantum biochemistry is developing at the junction between quantum mechanics, chemistry, and biology. For this reason, it is important to reach conclusions based on calculations for BAC in such a way that they can be understood by the majority of those who work in these fields. Problems concerning computational methods can be understood only by specialists. The results described in the language of the simplified MO theory may be accessible to a fairly large number of organic chemists and physical chemists capable of understanding the result of a theoretical study provided that it is presented in the form of the formula

of a chemical compound. Clearly, absolute conclusions about the best structure of the BAC are apparently not to be expected from specialists in the field of quantum chemistry. However, on the basis of calculations, it is possible to discover a fairly narrow range of several potentially active compounds and to employ them subsequently for experimental tests. At the present time, the majority of quantum-chemical studies concerning calculations on ATC have not as yet yielded practical conclusions. However, in many scientific centres, where there is close contact between theoreticians and experimenters, the structure–activity correlations based on RI already constitute a working instrument in the primary prediction of new active structures.

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# The Structure of the Active Centres and Stereoregulation in the Ionic-Coordination Polymerisation of α-Alkenes and 1,3-Dienes on Ziegler-Natta Catalysts

K.S.Minsker, M.M.Karpasas, and G.E.Zaikov

The development of theories of the mechanism of the stereospecific polymerisation of α-alkenes and dienes on Ziegler-Natta catalysts has been examined. Theories of the formation and structure of the active centres, the role of the heterogeneous component of the catalyst, the mechanism of chain initiation and growth, and the mechanism of stereoregulation in the polymerisation of alkenes and dienes have been discussed.
The bibliography contains 115 references.

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## I. INTRODUCTION

An important contribution to the development of the chemical kinetics of processes including polymerisation and polymer degradation was made by Academician N.M.Emanuel'. In his work, particular attention was paid to the study of radical reactions, and also reactions involving complexes and various ionic coordination compounds†.

Ziegler–Natta catalysts involving the salts of metal groups IV–VIII and organic compounds of groups I–III of Mendeleev's periodic system of the elements have been used for more than 30 years for the industrial production of stereoregular polymers of a number of α-alkenes and dienes. There is still lack of agreement, however, on the mechanism of polymerisation and stereoregulation in the presence of these catalysts. The present review examines existing theories in this field.

The following abbreviations are used: M represents a metal from groups I–III, M′ a transition metal, $\bar{P}$ the degree of polymerisation, OMC an organometallic compound, OAC an organoaluminium compound, MA a macromolecule, AC an active centre, PAC an active centre at the physical adsorption stage, CAC a chemical adsorption centre (a potential polymerisation AC), and MO a molecular orbital.

† N.M.Emanuel, G.E.Zaikov, and Z.K.Maizus, "Oxidation of Organic Compounds: Medium Effects in Radical Reactions", Pergamon Press, Oxford, 1984, 645 pp.

## II. NATURE OF THE ACTIVE CENTRES AND MECHANISM OF POLYMERISATION

### 1. Empirical Schemes

One of the first mechanisms, namely the stepwise anionic reaction mechanism, was proposed for the process in 1955 by Ziegler and co-workers.[1] The scheme is based on the following reactions: 1) the stepwise addition of the OAC to the alkene, and 2) the displacement of the Al atom from the alkene chain with the participation of $TiCl_4$ (al = 1/3 Al), which controls the ratio of reactions (1) and (2) in scheme 1:

Scheme 1

$$R(CH_2{-}CH_2)_n\text{al} + C_2H_4 \rightarrow R(CH_2{-}CH_2)_{n+1}\text{al} \qquad (1)$$

$$R(CH_2{-}CH_2)_{n+1}\text{al} \xrightarrow[TiCl_4]{C_2H_4} R(CH_2{-}CH_2)_n{-}CH{=}CH_2 + RAl \qquad (2)$$

This mechanism was very quickly rejected. In particular, according to Ref.1, more easily ionised OMC (Na or K pentyls) should form more active catalytic systems than $R_3Al$. This does not agree with the experimental data, however. Moreover, according to the Ziegler mechanism, the individual OMC should also bring about the polymerisation of α-alkenes to macromolecular polymeric products, but this does not take place. There are many other examples where the Ziegler theory does not agree with the experimental data, in particular the reliably established fact that the transition metal–carbon bond plays an active role in chain growth.

In the period 1955–1960, a large number of papers were published, which not only discussed the anionic mechanism[2-4] but also successively put forward the ionic-coordination,[5-18] free-radical,[19-21] cationic,[22,23] and radical-ion[24-26] mechanisms for the process.

The free-radical mechanism, based on the reactions:

$$R_3Al + TiCl_4 \rightarrow RTiCl_3 + R_2AlCl$$
$$RTiCl_3 \rightarrow R^{\cdot} + TiCl_3$$

was also quickly rejected, since it did not explain many fundamental experimental data, in particular the following: a) radical chain transfer agents do not influence $\overline{P}$ for the polymers, b) familiar inhibitors of free-radical reactions have a positive influence on the process (the reaction rate, $\overline{P}$, and the stereospecificity of the process increase), c) change in the nature of the components of the Ziegler–Natta catalyst generally leads to a change in the reactivity of the monomers in copolymerisation, d) the time of existence of the growing MA is much greater than that in free-radical polymerisation, e) the formation of "live" polymer chains is possible,[27–30] etc.

The cationic mechanism was also rejected, even if only because the order of activity of the monomers in complex formation with Ziegler–Natta catalysts (butadiene > isoprene > styrene > isobutylene > α-methylstyrene) differs markedly from the order of the activities of these monomers in their reaction with Lewis acids.

The ion–radical mechanism:

$$A^{\cdot} + C_2H_4 \rightarrow A{-}CH_2{-}CH_2^{\cdot} \rightleftarrows A^{+-}CH_2{-}CH_2^{\cdot}$$
$$A^{\cdot} = \text{radical}$$

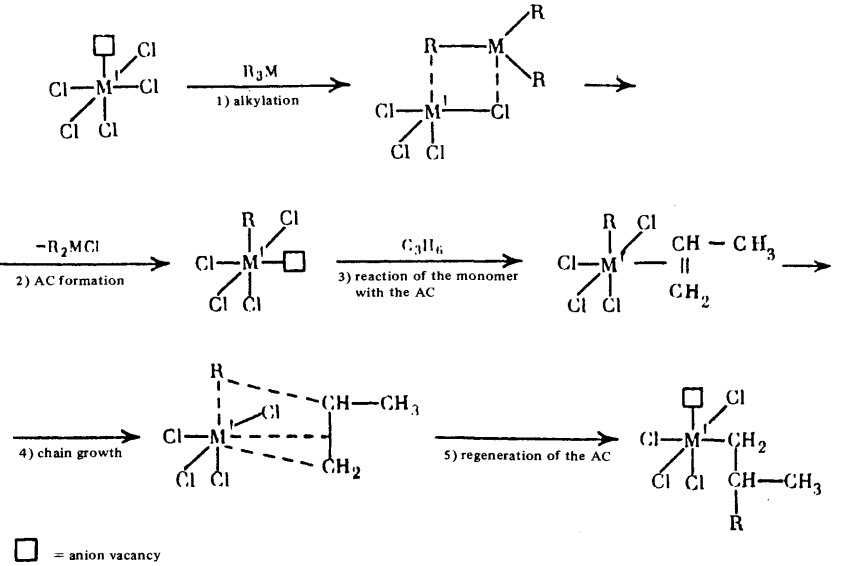
also does not agree with many of the above experimental data. This mechanism does not explain the chain termination associated with the removal of the MA from the catalyst surface, or the presence in the MA of organic groups previously present in the OMC.

Beginning in the nineteen-sixties, various versions of the ionic-coordination mechanism of polymerisation on Ziegler–Natta catalysts, which takes account of the important role of the reaction of the OMC with the M′ salts in the production of the AC, were accepted, and for more than 20 years now, two theoretical schemes have coexisted and been widely discussed, based on: a) the single-metal model of the AC,[4,16,17,31–49] etc., and b) by two-metal model of the AC,[2,5,7–11,13–15,18,50–61] etc.

*a) Single-metal Model of the Active Centre*

Without going into details of all the proposed schemes, it can be stated that the single-metal model of the AC includes the alkylation of M′ without a change in its oxidation state. Chain initiation and growth in the polymerisation take place by the insertion of the alkene at the M′–C bond. The specific feature of the mechanism of polymerisation on Ziegler–Natta catalysts is that all the stages controlling the process, that is the initiation, growth, and all forms of limitation of the chains, involve highly active alkyl radicals, forming weak covalent bonds with M′.

The essential features of the process are most fully reflected by the Cossee–Arlman scheme.[17,33,34] According to this scheme, the active beginning of the polymerisation is due entirely to M′ and its ligands. On the edges of the $M'X_n$ crystals, AC are formed, having one anion vacancy in the octahedral coordination sphere of M′. The coordination of the monomer to the AC leads to the rupture of the C=C bond and the insertion of the monomer at the M′–C bond. The migration of the gorwing chain restores the complex to its original state, so that the addition of the next monomeric unit becomes possible:



The fact that the OMC of the most electropositive metals are suitable for obtaining active catalytic systems is due to their high alkylating power.

During growth, the chain oscillates between two positions on the $(M')^{n+}$ ion, increasing by one unit each time. In the Cossee–Arlman scheme as modified by Rodriguez and Van Looy,[59] the migration of the growing MA is not regarded as essential.

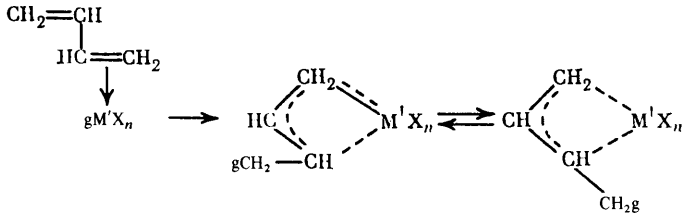
Later papers, for example Refs.36–40, while retaining the main ideas of Cossee given above, examined individual aspects of the problem in more detail. In particular, it was suggested[39] that the catalytic process is not a purely surface phenomenon, and that all the M' atoms take part in the reaction. The use of $(TiCl_3.AlCl_3)$–$R_2AlCl$ leads to the production of the characteristic crystal structure of $Ti_8Cl_{24}.Al_2Cl_6$, which contains cavities whose dimensions allow $R_3Al$ and the monomer to diffuse to M'. $R_3Al$ alkylates $TiCl_3$, after which the process develops according to the Cossee–Arlman scheme.[33]

In Ref.40, a general mechanism was proposed for both the polymerisation of the monomers and the metathesis processes (see Ref.62).

Dolgoplosk and co-workers[36–38] suggest that in the polymerisation of dienes the initiation involves a π-allyl complex in the *anti*-conformation. The diene takes part in the process almost always as a bidentate ligand:

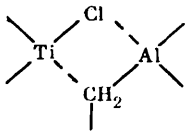
If however the AC has only one anion vacancy, the diene can coordinate only through one C=C bond in the trans conformation:

Scheme 3

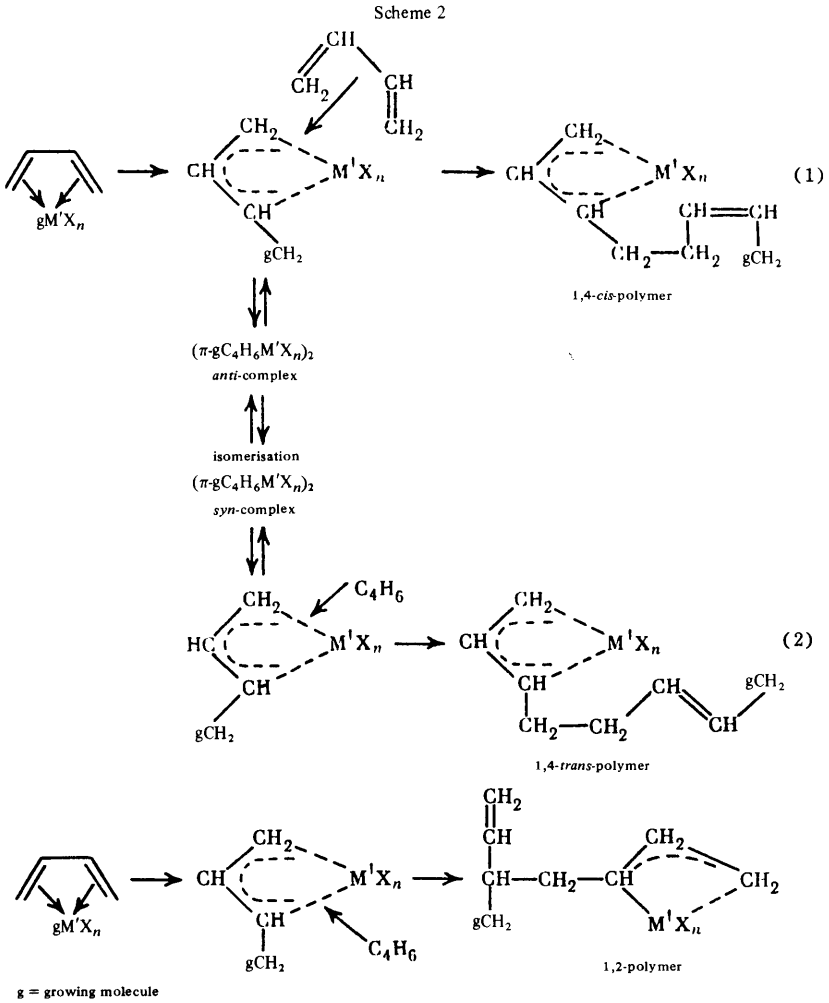


*b) The Two-metal Model of the Active Centre*

The polymerisation mechanism for the two-metal model of the AC assumes the existence of complexes formed by the M' salt and the OMC, of the type



Scheme 2



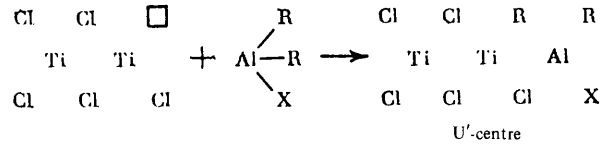
The polymerisation involves the formation of a complex by the catalyst with the monomer. Since the electropositive nature of the atom M′ increases with decrease in its oxidation number, only compounds of M′ with low oxidation numbers can show catalytic activity. The $(M')^{n+}$ cation initiates the process, and the negatively charged ionic complex of the

OMC ($R_3^-$, $-\overset{|}{\underset{|}{Al^+}}$) brings about the growth of the MA.

According to Refs.7, 11, 19, 52, etc., chain growth takes place in the surface layer of the crystal lattice of a mixed salt of M′, in particular $TiCl_3.R_2AlCl$. The role of $TiCl_3$ reduces to the activation and stabilisation of the OAC, and the negatively charged $R^{\delta-}$ group initiates the "unwinding" of the MA from the Ti atom, which forms a complex with the monomer molecules.

According to Refs.11 and 18, the reaction of the heterogeneous ($M'X_n$) and homogeneous ($R_mM$) components gives impurity crystals containing surface electronic defects of the "colour centre" type. One route for their formation involves the chemisorption of the OMC on the ionic lattice of the M′ salt ($R_3Al$ on $TiCl_3$), primarily in the positions of existing crystal defects.

Real crystals of M′ halides (the heterogeneous component of the Ziegler–Natta catalysts) always have an excess of negative charge. The chloride ions are removed more easily from the edges of the crystalline plate than from its centre.[33] As a result, in real crystals the Cl vacancies are situated at the edges of the crystals and in the positions of the dislocations, where polymerisation takes place preferentially.[64,65] Thus the crystal lattice of $TiCl_3$ is completed by the cationic fragment $R_2Al^+$, which is formed from $R_3Al$ in the field of the surface $Cl^-$ anions. An impurity crystal is formed. Since crystals of this type are essentially ionic systems, for which it is advantageous to remain electrically neutral, this requires the "formation", conjugated with the above process, of a vacancy in the region of which $R^-$ is localised. In the process, on the one hand, the anion defect is "saturated", and on the other hand the unstable $R^{\delta-}$ is stabilised. The crystal lattice defect produced—a potential polymerisation AC—is called a U′-centre:[11,18]

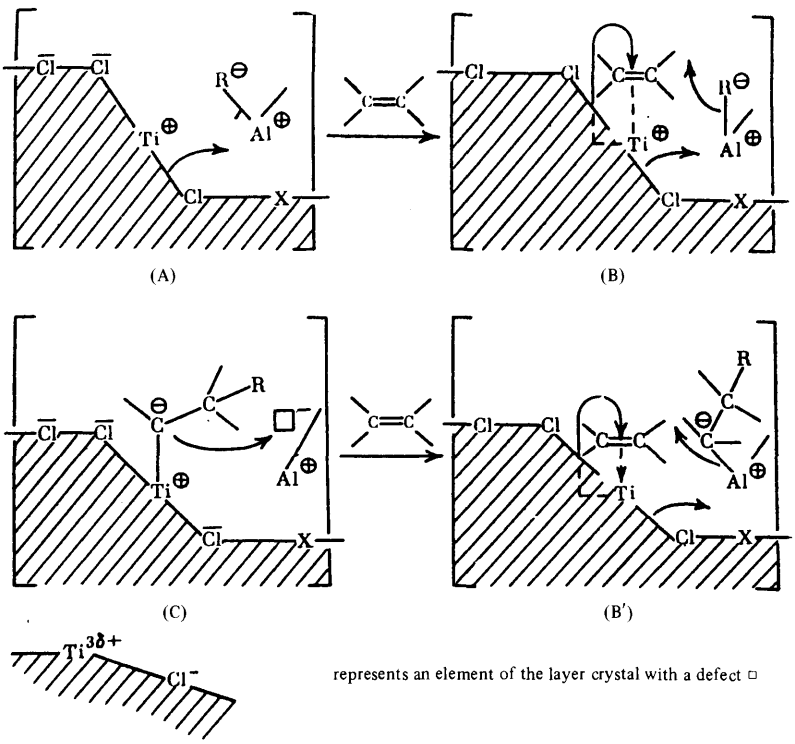



U′-centre

The polymerisation always involves the formation of a ternary complex $\rangle C{=}C\langle .M'X_n.R_nMX_{3-n}$ ($n$ = 3–1), so that the heterogeneous component should be capable of forming a complex not only with the OMC but also with the monomer. In the case of ionic solids, the adsorption capacity is related to the defect nature of their structure and depends on temperature, the concentration of foreign impurities in the form of other structural defects which can take part in electronic processes, etc.

The monomer, chemisorbed on the potential AC, reacts with M′, which contains partly filled *d* orbitals (for example Ti), to form a molecular complex similar in character to the familiar π-complexes of alkenes with Pt, Cu, and Ag.[18]

The reaction of $M'Cl_n$ with the monomer takes place by a donor–acceptor mechanism, and that with the OMC by an acceptor–donor mechanism to give an impurity ionic crystal. As a result, $R^{\delta-}$ of the OAC acquires an increased negative charge. Electron transfer becomes possible through the closed system:[18]



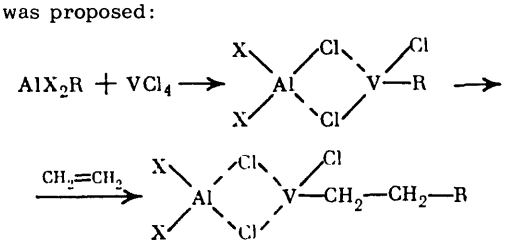

represents an element of the layer crystal with a defect □

The scheme assumes simultaneous electrophilic and nucleophilic attack on the monomer molecule by the components of the catalytic complex, so that the heterogeneous catalytic polymerisation of alkenes and dienes under the influence of Ziegler–Natta catalysts can be regarded as "push–pull" reactions, involving the successive introduction of the monomer, its coordination, attack by $Ti^{3+}$ and R–Al$<$, and insertion at the Ti–C bond to give the MA, that is the operating principle of an automatic conveyer is established. As a result of cooperative synchronous electron transfer processes (the "concerted" mechanism), a σ-bond is formed between a carbon atom of the $R^{\delta-}$ group and a neighbouring carbon atom of the monomer. The group R, belonging initially to the OAC, becomes the terminal group in the MA formed; this leads to the reappearance of an active group $R^{\delta-}$, larger by one monomer unit, and localised on the anion vacancy, and the AC is regenerated.

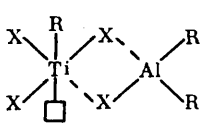
In this scheme, the nature of the interaction of the catalytic system and the monomer, and also the stability of the ternary complexes formed, should naturally be influenced by all the parameters characterising the heterogeneous component, and also its structural-chemical features, in particular the crystallographic radius, the magnitude of the charge, the ionisation potential of $(M')^{n+1}$, the crystal lattice structure, etc., and this is confirmed by a large amount of experimental data. An important role is also played by the atomic radius of M, the polarity of the M–C bond in the OMC, the chemical nature and structure of the monomer, the electron affinity of the monomer, polar and steric factors, etc.

These ideas are consistent with practically all the experimental data, including the effect of the modification of Ziegler–Natta catalysts by ethers, amines, sulphides,[27,28] aromatic compounds,[66,67] oxygen, and peroxides,[30] and are fairly universal. (By ignoring various features, it is possible to arrive at the schemes mentioned above, proposed in Refs.1, 6, 9, 10, 14, 15, 17, 57, 58, etc.).

In the polymerisation mechanism schemes described above, based on the two-metal model of the AC, it is assumed that both the atoms M′ and M are in the first coordination sphere of the AC. In some papers[60,61,68–70] it is postulated that M′ is in the second coordination sphere of the AC# and influences the polymerisation only through the electronic structure of the complex formed. For example, in Ref.70 the following scheme was proposed:



A similar viewpoint is held by the authors of Refs.60 and 61, who proposed the following AC structure:



They do not however take account of the fact that in heterogeneous systems, AC of this type probably cannot be formed.

Thus the first, almost twenty-year, period of the study of various aspects of the chemistry and technology of polymerisation on Ziegler–Natta catalysts is characterised by the appearance of a large number of different empirical schemes, but often without detailed consideration of the problem and observation of the fundamental requirement that the theoretical postulates correspond to all the available experimental data. It is therefore possible to exclude from consideration the purely ionic, radical–ion, and free-radical polymerisation mechanisms. The examination of ionic–coordination polymerisation on Ziegler–Natta catalysts is now based essentially on one of the two concepts of single-metal or two-metal catalysis, differing in the structure of the AC and the mechanism of the process.

Up to the present, the Cossee–Arlman scheme (Refs.41 to 49, etc.) with a single-metal model of the AC has been most popular. At the same time, its fundamental unsatisfactory features are well known. This scheme: a) does not make specific the role of the OMC in the regulation of the activity and stereospecificity of Ziegler–Natta catalysts; b) does not explain why in many cases the OAC influences the activity and stereospecificity of the catalysts, and why organozinc compounds, which are good alkylating agents, give less active and less stereospecific active centres; c) does not explain why electron-donor ligands (amines, arenes) improve considerably the activity and stereospecificity of Ziegler–Natta catalytic systems; d) does not explain why only a small proportion of the alkylated M′ starts polymer chains, etc. Another weak feature of the scheme is the oscillating migration of the growing MA chain during polymerisation.

An attempt has been made[59] to eliminate these unsatisfactory features of the Cossee–Arlman scheme while retaining its basic postulates; its was suggested that the AC is a four-coordinate alkylated M′ atom with two anion vacancies, one of which is subsequently occupied by the OAC. This treatment, however, leads essentially to the fundamentally different two-metal AC structure.

Thus early empirical schemes, based entirely on a logical analysis of experimental data and general theoretical postulates, have not produced a satisfactory simple theory of the mechanism of catalysis in polymerisation on Ziegler–Natta catalysts. In a short period of time (less than 10 years) quantum-chemical studies have provided a deeper understanding of the problem.

## 2. Present-day Trends

The principal unsatisfactory features of early empirical theories of the mechanism of polymerisation on Ziegler–Natta catalysts are a restricted approach to the solution of the problem, the hypothetical nature of the choice of the AC model, the neglect of the characteristic features of the structure of the heterogeneous component, etc. This explains the development of a large number of theories and the lack of unambiguous solutions, and it should be borne in mind that it is impossible to determine the mechanism of polymerisation on Ziegler–Natta catalysts using only existing experimental methods.

Although the single-metal AC model appears simpler, it is being used and developed intensively. There are however no grounds for neglecting the two-metal AC model, which provides a much more convincing interpretation of the mechanism of polymerisation on Ziegler–Natta catalysts in sufficiently good agreement with practically all experimental data, many of which cannot be explained by other hypotheses, including the Cossee–Arlman single-metal catalysis scheme.[17,33,34]

#Particularly in the case of homogeneous Ziegler–Natta catalysts.

The following reliable and generally accepted experimental facts must always be borne in mind: a) the AC are formed only by the reaction of both components of the catalytic system; b) all stages of the catalysis involve the M′ atom and the surrounding ligands, and the M compounds; c) the polymer chain grows in "hairlike" fashion, and one of the substituents R of the OMC molecule is situated at the end of the MA being formed; d) the rate of the process and the structure of the polymer are determined by the nature of not only M′ but also the OMC, that is by the structure of the AC, which in turn depends on the nature of the ligands in the coordination sphere (monomer, counter-ion, co-catalyst, modifying additives, solvent, and any other added reagent with electron-donor or electron-acceptor properties); e) the oxidation state of M′ (Ti, V, Cr) in the AC is generally 3+; f) the growing MA are arranged in spirals and are concentrated chiefly on the side faces and dislocations at the points where the M′ ions appear on the crystal surface; g) polymerisation on Ziegler–Natta catalysts is characterised by relatively low activation energy values ($E_{act}$).

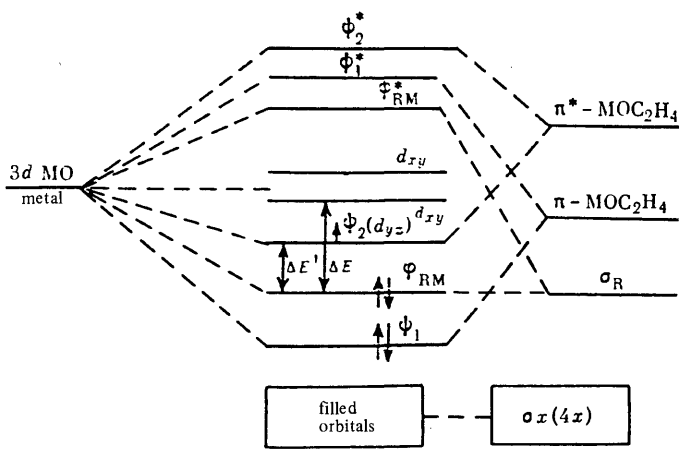
At the same time, many problems of specific polymerisation under the influence of Ziegler–Natta catalysts cannot be solved experimentally by existing methods. This applies particularly to the structure of the AC, the separate stages of chain initiation, growth, and termination, etc. A number of fundamental problems can be solved by combining experiment with modern methods of calculation and process modelling using the techniques of quantum chemistry, numerical experiment (monte Carlo, molecular dynamics), etc.[17,68,69,71–108]

*a) Modelling the Process of Polymerisation on Ziegler–Natta Catalysts*

The determination of the mechanism of ionic–coordination polymerisation on Ziegler–Natta catalysts is directly related to the determination of the structure of the AC.

A characteristic feature of the first studies[71–75] was the investigation of various particular problems regarding AC, selected according to the subjective opinions of the research workers. The mechanism of polymerisation on both single-metal[17,76–85] and two-metal[68,69,75,86–96] AC was examined.

*Single-metal model of the active centre.* The first paper applying quantum mechanics to polymerisation on Ziegler–Natta catalysts was published by Cossee.[17] It examined a simplified molecular diagram of an octahedral alkylated complex $M'Cl_4R$ and ethylene:




In the formation of the complex of the alkene with $RTiCl_4$, $\Delta E$ in the diagram corresponds to the energy which must be acquired by the electron taking part in the antibonding of the Ti–C bond. A high value of $\Delta E$ facilitates the preservation of the Ti–C bond in the absence of the alkene. When the alkene is bound in the complex, the interaction of the *d* orbitals of M′ and the $\pi^*$ antibonding orbitals of the monomer produces a new energy level $\psi_2(d_{yz})$, which lies below the energy level of the 3*d* orbital of the original M′, and the excitation of the electron of the M′–C bond ($\phi_{RM}$) can take place much more easily. The Ti–C bond therefore readily undergoes homolysis. If $\Delta E'$ is smaller than the difference in the critical energies,[97] the R group is "ejected" as a radical, which in a coordinated process subsequently adds on to the nearest carbon atom of the alkane. At the same time, a C atom of the alkene adds on to M′. When the reaction is repeated, the R group returns to its original position. According to Cossee's model,[17] only some M′ ensure the necessary conditions for the process. According to the MO diagram, for the M′ compound to show catalytic activity it is not essential to have an electron in each of the orbitals $d_{yz}$, $d_{xz}$, and $d_{zy}$. The $\psi_2(d_{yz})$ orbital, however, must not contain two electrons simultaneously. This means that only $(M')^{n+}$ ions having 0–3 unpaired *d* electrons are suitable as catalysts. The specific action of the M′ ion is possible only when the 3*d* level of M′ lies between the bonding and antibonding energy levels of the alkenes. Later analogous MO studies[77] of the complexes $CH_3TiCl_3$, $CH_3TiCl_4$, $CH_3TiCl_4.CH_2{=}CH_2$ by the Wolfsberg–Helmholz–Ballhausen method added nothing new to these ideas.

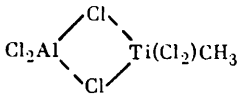
In Ref.76, the Hückel extended iteration method was used to study the migration of the $CH_3$ group to a coordinated ethylene molecule on the signle-metal AC $Ti(Cl/2)_4CH_3$ and to confirm the data of Ref.17; thus the *d* level of M′ lies between the $\pi$ and $\pi^*$ levels of ethylene, the bonds between R and the Ti atoms are localised, and the corresponding levels lie only 16000 $cm^{-1}$ below the non-bonding $d_{xz}$ and $d_{yz}$ orbitals of M′. The chief difference between the Ti–C bond and the Ti–Cl bond lies in the much lower electronegativity of the two interacting atoms (the overlap integrals are the same in both cases). The results of the calculation indicated that the low kinetic stability of the Ti–C bond is due to the small energy difference between the MO bonding M′ to C and the unoccupied *d* orbitals.

Subsequent studies cast doubt on Cossee's conclusion that the driving force of the reaction is the decrease in the strength of the Ti–C bond resulting from the manifestation of $\pi$-acceptor properties by the alkene on coordination to M′.[41,42] The process of polymerisation on the Ziegler catalytic systems $[CH_3TiCl_4.C_2H_4]^n$ (the charge $n$ = 0, −1, −2) and $Ti(CH_3)Cl_3.C_2H_4$ was studied on the basis of Cossee's scheme using CNDO and SCF $X_\alpha$-SW methods.[78–80] The assumption that there is extensive overlap of the $3d_{yz}$ orbital of Ti and the $\pi^*$ orbital of ethylene, which is the basis of many postulates of Cossee's theory, and hence of the driving force of the polymerisation reaction, was not confirmed. Moreover, according to Ref.78, Cossee's polymerisation mechanism can apply only in particular cases. The results obtained in Refs.78–80 agreed with the results of quantum-chemical studies assuming a two-metal model for the AC.[68,69]

Semi-empirical MO calculations of a hypothetical reaction path assuming that intermediate compounds of the metallocyclopentane type are formed in the polymerisation of alkenes were carried out in Ref.79. It should be noted, however, that the polymerisation scheme proposed in Ref.79 is not consistent with the experimental data.

The concept of the single-metal catalysis of polymerisation on Ziegler–Natta catalysts was developed systematically in a recent series of papers.[81–85] In these studies, the CNDO/2 and MINDO/3 methods were used to study the complexes $[RTiCl_4]^{2-}.C_2H_4$ (Cossee's AC model) and $Al(CH_3)_3.C_2H_4$, $AlH_3.C_2H_4$, and $(CH_3)_2AlH.C_2H_4$. The latter were chosen to investigate the general regular features of the catalytic transformations of α-alkenes. The studies gave the following results: a) a two-stage reaction path involving the formation of a π-complex by the alkene with the Ti ion is energetically favourable; b) the insertion stage requires only a small $E_{act}$ and is accompanied by the formation of a stable *cis*-configuration of the alkyl and the growing MA; after the insertion of the monomer, *cis–trans* isomerisation is possible; c) the limiting stage is the coordination of the alkene with rearrangement on the AC of the growing end of the MA under the influence of the coordinated monomer; d) a stable AC structure is formed by a Ti ion with four octahedrally arranged $Cl^-$ ions and one R group. The activation energy of the stages involving the coordination and insertion of the monomer with the participation of the AC is made up of the energy of rupture of the π-bond of the alkene and the energy required to change the coordination state of the AC. An analysis of experimental data on the polymerisation of alkenes on the individual compounds $M'R_n$ or $M'X_m.R_{n-m}$ (R = methyl, benzyl, neopentyl, tetramethylallyl, or allyl; X = halogen or cyclopentadienyl) also established[85] that the presence of a M'-C σ-bond in the individual compounds is not a sufficient condition for their catalytic activity in the polymerisation of alkenes. Particular importance is assigned to the coordination state of $M'X_mR_{n-m}$ ($M'R_n$). It is only when octahedral structures are formed in the AC–alkene complexes that sufficiently stable π-complexes can be produced on the AC. Data from other papers were also confirmed: in single-metal Ziegler catalysis, the $3d-\pi^*$ molecular orbital overlap is extremely slight, and the Ti–C bond is determined almost entirely by the highest bonding orbital of the alkene complex.[81–85]

*The two-metal model of the active centre.* In one of the first papers,[68] the polymerisation of ethylene under the influence of a homogeneous catalytic system was studied by the CNDO method.

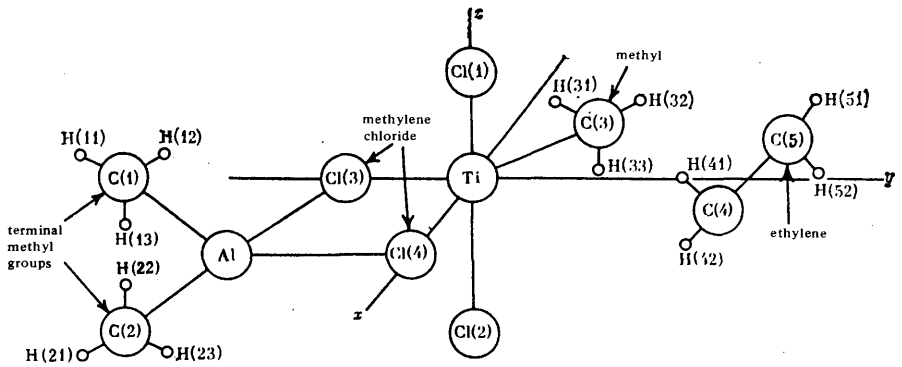



It was found that there is comparatively little perturbation of the electronic structure of ethylene in the complex, and extensive polarisation of the Ti–C bond. The authors cited assume that the R group and the monomer, at all microstages of the growth of the polymer chain, can remain joined to the Ti atoms, and that practically no energy is required for the rupture of the bonds. The driving force of the displacement of the $R^{\delta-}$ group may be the reaction of the slight positive charge in the monomer (in the complex) and the fairly strong negative charge of the terminal C atom of the R group (the growing chain). Comparision of the intermediate π-complex of ethylene and the compound formed by the insertion of the monomer shows that the energy of the complex not containing the alkene is lower. The optimum structure in this case is a trigonal bipyramid without a vacant position. Thus when the alkene is coordinated to the AC, rearrangement of the complex takes place to give a trigonal bipyramid–octahedron, accompanied by the production of a vacant position. The energy required for the rearrangement can be regarded as $E_{act}$ for the chain growth reaction.

The results of the calculations led to some general conclusions:[68] 1) the high activity of Ziegler–Natta catalysts in the polymerisation of alkenes is due to the increased lability of the C–M' bond in the AC compared with typical ionic AC and to the geometry of the complex of the monomer with the AC, favourable for the insertion of the alkene at the C–M' bond, 2) the contribution of the dative interaction of the $Ti^{3+}$–alkene bond is slight, and there is little $3d-\pi^*$ orbital overlap, 3) the properties of the $Ti-CH_3$ bond are determined almost entirely by the highest bonding orbital of the alkene complex (the contribution of the Ti atom to this bond is practically associated only with the *d* orbitals of M'), and 4) the OAC has no significant influence on the energy levels of the AC, which are of decisive importance for the polymerisation process. The role of the OAC when soluble catalysts are used reduces to the stabilisation of an AC structure with a high coordination number for the $M'(Ti^{3+})$ ion as a result of the formation of bridging bonds between M and M'. It should be noted, however, that the last conclusion is not completely correct, and that the function of the OAC in ionic–coordination catalysis is probably more varied (Refs.11, 71, 75, 86, 87, 93, 95, etc.).

The results of a study[96] of polymerisation in the presence of homogeneous Ziegler–Natta catalysts ($Ti(OCH_3)_4-R_3Al$) practically coincided with the conclusions reached in Ref.68.

A non-empirical SCF LACAO MO method (the restricted Hartree–Fock (RHF) method)[69] was used to carry out a calculation for the reaction $TiCl_4 + (CH_3)_3Al + C_2H_4 \rightarrow TiCl_4.(CH_3)_3Al.C_2H_4$, modelling the polymerisation of alkenes on Ziegler–Natta catalysts.

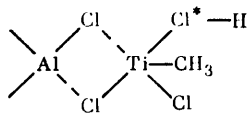


According to the calculation, the polymerisation takes place in three main stages: 1) the coordination of ethylene to $TiCl_4(CH_3)_3Al(AC)$, accompanied by the transfer of the $CH_3$ group of the AC from the trigonal position originally occupied to an octahedral position, 2) the reaction of ethylene with the $CH_3$ group of the AC and the rupture of the π-bond of ethylene, and 3) the formation of the MA. Following Refs.11 and 17, a "concerted" mechanism of polymerisation is assumed.

Unfortunately, the authors of Ref.68, 69, and 96 ignored the equally well argued model of the two-metal AC, according to which the cocatalyst (or a fragment of it) is situated on the same side of the M′ atom as the growing chain and the monomer coordinated to the AC. This version is possible in both homogeneous and heterogeneous Ziegler–Natta systems.

The two-metal model of the AC has been used in a series of interesting papers.[71,75,93–95]

The unrestricted Hartree–Fock (UHF) method in the CNDO approximation with allowance for configuration interaction (CI)§ has been used to study the homolysis of the metal–carbon σ-bond in OMC of Ti and Al atoms. A model was proposed, explaining from a single viewpoint the at first sight contradictory data on the relative stability, thermal stability, and reactivity of the M–C bond in different OMC. A fundamental difference between the Ti and Al atoms is the ability of M′ to change its oxidation state with relatively slight deformation of the M′–C bond. The decisive factors in this case are not only the similarity in the energies of the *s*, *p*, and *d* atomic orbitals but also the less diffuse character of the *d* atomic orbitals compared with *s* and *p* orbitals. For the same excitation energy, this rearrangement ensures greater deformations of the M′–C bond and facilitates the formation of a partly bound alkyl ligand, capable of taking part in subsequent concerted processes in the coordination sphere of M′. The magnitude of $\Delta E_{S_0 \to T_j}$ (the energy of the transfer to the lowest triplet excited electronic state) in compounds of the same type formed by a given M′ correlates with the relative elongation of the bond after which the change in the oxidation state of M′ begins. The lower $\Delta E_{S_0 \to T_j}$, the more labile the Ti–C bond, that is $\Delta E_{S_0 \to T_j}$ can be used as an indication of the reactivity of the OMC. The AC most probably have a two-metal structure:



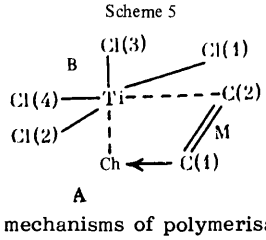

It is assumed that there is no coordination vacancy on the Ti atom. The alkene displaces the saturated fragment $C_\gamma RR^*$ of the growing MA, overcoming the energy barrier to insertion at the Ti–R bond. Preference for the AC with a two-metal structure is also observed for homogeneous Ziegler–Natta systems: $L_2TiRCl.AlCl_3$ (L = Cp, Cl; R = Cl, $CH_3$, $C_2H_5$, $C_4H_7$).[95] The activity of the Ti–C bond in catalysis is due to the ease of formation of a "quasi-octahedral" structure by the Ti atoms in the complex.

§For comparison, the same calculations were repeated by the restricted Hartree–Fock (RHF) method, widely used in quantum-chemical calculations for coordination–ionic polymerisation. It was noted that the observed change in the oxidation state of M′ with deformation of the σ-bond (UHF calculation) cannot be detected by the usual quantum-chemical methods taking no account of the dynamics of the correlation contribution to the energy (RHF method without allowance for CI).

Unfortunately, Refs.71, 75, and 93–95 gave no answer to the question of the geometric structure of the AC and the mechanism of polymerisation on Ziegler–Natta catalysis.

Thus modern methods for studying the ionic–coordination polymerisation of α-alkenes and dienes by quantum-chemical methods have made it possible to extend theories of the characteristic features of the electronic structure of the assumed AC and the catalytic complexes formed with and without the participation of the monomer, and also to refine various details of the mechanism of the polymerisation processes. At the same time, the studies carried out are not free from serious defects. In particular, in most studies the structure of the AC (single-metal or two-metal model), as already noted, is assumed in advance in accordance with the subjective opinions and tastes of the authors. The calculations, particularly those relating to the stage of AC formation, generally did not take account of the characteristic features of the structure of the surface of the heterogeneous component of the catalysts, and the position of the OMC was not studied, and was usually assumed *a priori* (before the calculations). These are essentially incorrect assumptions. It is sufficient to note that the phase state of the catalyst and the position of the OMC influence the steric environment of the AC being formed and their electronic structure, so that stereoregular polymers, for example isotactic polyalkenes, are formed in heterogeneous systems, whereas syndiotactic or atactic polyalkenes are formed in homogeneous systems with similar compositions. It may be stated that the use of quantum chemistry has shown that the two-metal model is highly probable. This is confirmed, in particular, by the results of a study[86] of the polymerisation of ethylene by the CNDO method. Two AC models, the single-metal model of Cossee[17] and the two-metal model (scheme 4 [18]), were compared under identical conditions. The authors examined the stages of coordination and insertion of the monomer (M) (shown by the arrow in scheme 5 below), in the course of which the monomer is displaced from the original coordination position into the position previously occupied by the chain, increasing by two carbon atoms the distance between the growing MA (Ch) and the Ti atom.

Scheme 5




A

Comparison of the mechanisms of polymerisation from the dependence of the energy of the system, the charges on the atoms, and the bond orders on the reaction coordinate indicates unambiguously a preference for the two-metal model of the AC,[11,18] according to which the cocatalyst ($R_3Al$) is on the same side of the Ti atom as the monomer and the growing MA (position A), compared with the single-metal AC model of Cossee,[17,33] in which $R_3Al$ is on the other side of the Ti atom from the monomer and Ch (position B). According to Ref.86, the growth of the MA most probably takes place with the participation of the $Al–R–Ti^{\delta+}$ group. The organoaluminium compound coordinated to Ti chloride takes direct part in the addition of the monomer to the growing chain by simultaneous nucleophilic (by $R–Al\lesssim$) and electrophilic by $Ti^{\delta+}$) attack on the monomer (the "concerted" mechanism), as previously assumed in Refs.11, 18, 69, 76, etc. The OAC plays an active role by stabilising the monomer on coordination to the AC, facilitates its introduction into the growing MA, and decreases $E_{act}$ for the polymerisation process.

### 3. Recent Progress

A distinguishing feature of papers published in the period 1980–1982 [87–92] was the combination of quantum-chemical calculations (in the CNDO approximation), empirical methods ("atom–atom" potentials), and numerical experiment methods (Monte Carlo). The dynamics of the formation of the AC produced by the reaction of organic compounds of M (Li, Na, Be, Zn, Mg, Al, etc.) with salts of M′ (Ti, V, Cr, etc.) were examined. In the calculations, account was taken of the real structure of the surface of the heterogeneous component of the catalyst. The polymerisation process was studied for a number of α-alkenes (ethylene, propene) and 1,3-dienes (butadiene, isoprene, piperylene, 4-methylpenta-1,3-diene, etc.).

The studies carried out have made it possible to determine much more reliably the characteristic features of the structure of the AC and the effect of stereoregulation in the polymerisation of α-alkenes and dienes in the presence of Ziegler–Natta catalysts.

#### *a) Structure of the Active Centres*

The process of AC formation by the reaction of the components of the catalytic system takes place in two stages. [87–91] In the first stage, at large intermolecular distances between the OMC and the crystal of the M′ salt, the reaction between the components of the catalytic system is due to Coulombic and dispersion forces; reversible physical adsorption takes place, accompanied by the orientation of the components of the Ziegler–Natta catalyst relative to one another without change in their structure, and the frequency with which the subsequent non-equilibrium stages of the reaction take place on a particular AC is proportional to the equilibrium population of this centre at the stage of physical adsorption.

The second stage is the chemical adsorption of the OMC on the crystal of the M′ salt. Here the principal role is played by exchange forces, which bring about a redistribution of the charges and a change in the structure of the interacting components. The process of chemical adsorption leads to the formation of the AC.

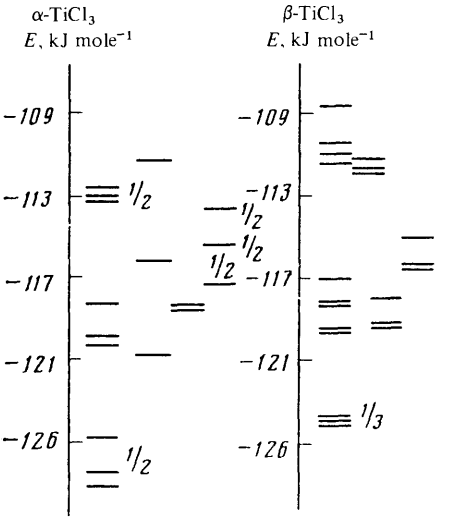



**Figure 1.** Energy level spectrum of the interaction of the physical adsorption of $(CH_3)_2AlCl$ on the surface of α- and β-$TiCl_3$.

For each system there are several types of physical adsorption centre with different energies (Fig.1) and structures (Figs.2 and 3). Among these it is possible to distinguish

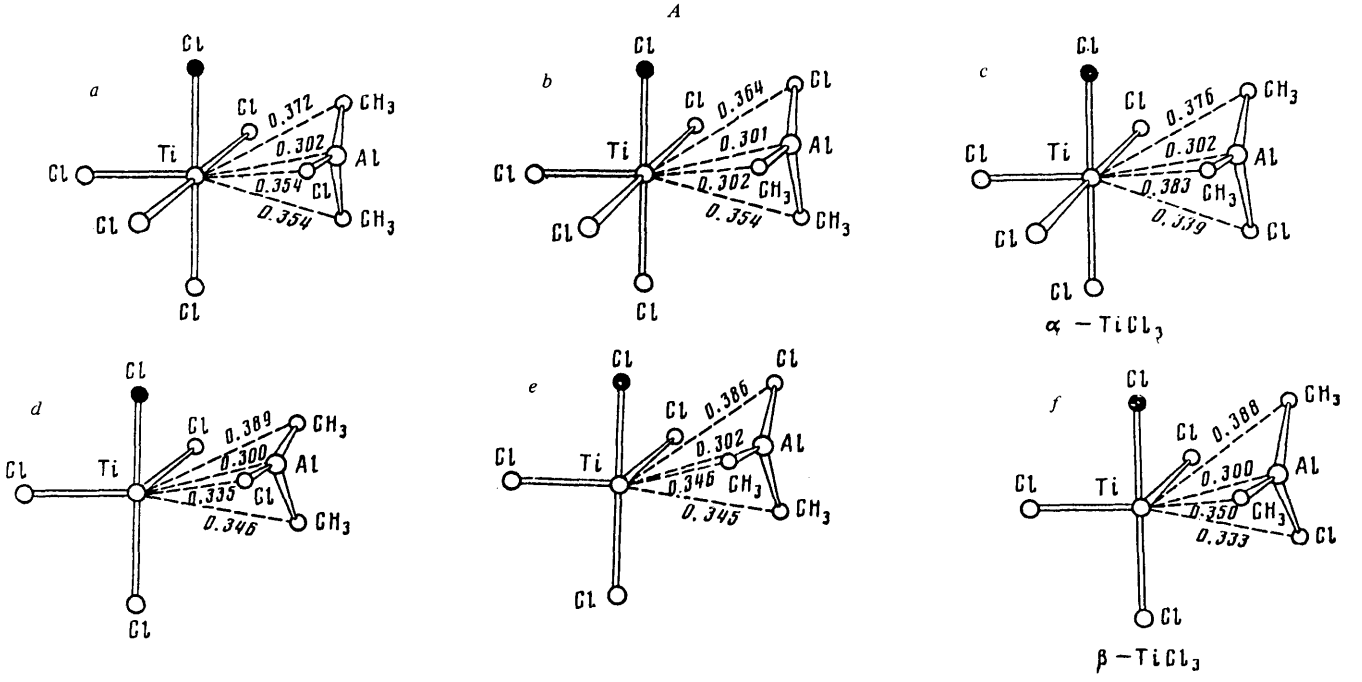



**Figure 2.** Structure of the physical adsorption centres of organometallic compounds on the surface of α- and β-$TiCl_3$ crystals (configurations corresponding to the energy minimum, distances given in nm): *A*) $Al(CH_3)_2Cl$ (*a–c*—PAC-1, *d–f*—PAC-2); *B*) $Be(CH_3)_2$, $Mg(CH_3)_2$ (*a,b,d,e*—PAC-1, *c,f*—PAC-2); *C*) $NaCH_3$ (*a–c*—PAC-3).

centres of the same type with identical three-dimensional structures: PAC-1 (physical adsorption centres formed mainly on the surface of the crystals of $TiCl_3$ and $VCl_3$), PAC-2 (β-$TiCl_3$, $CoCl_2$, $NiCl_2$), and PAC-3 ($CrCl_3$, $CoCl_2$, $TiCl_3$) (Figs.2 and 3). Estimation of the equilibrium populations (the relative concentration or proportions of different PAC) showed[87-89,91] that the populations (proportions) of the various specific PAC distinguished above are probably related to the yields of isotactic polyalkenes and *trans*-poly-1,4-dienes (PAC-1), atactic polyalkenes and

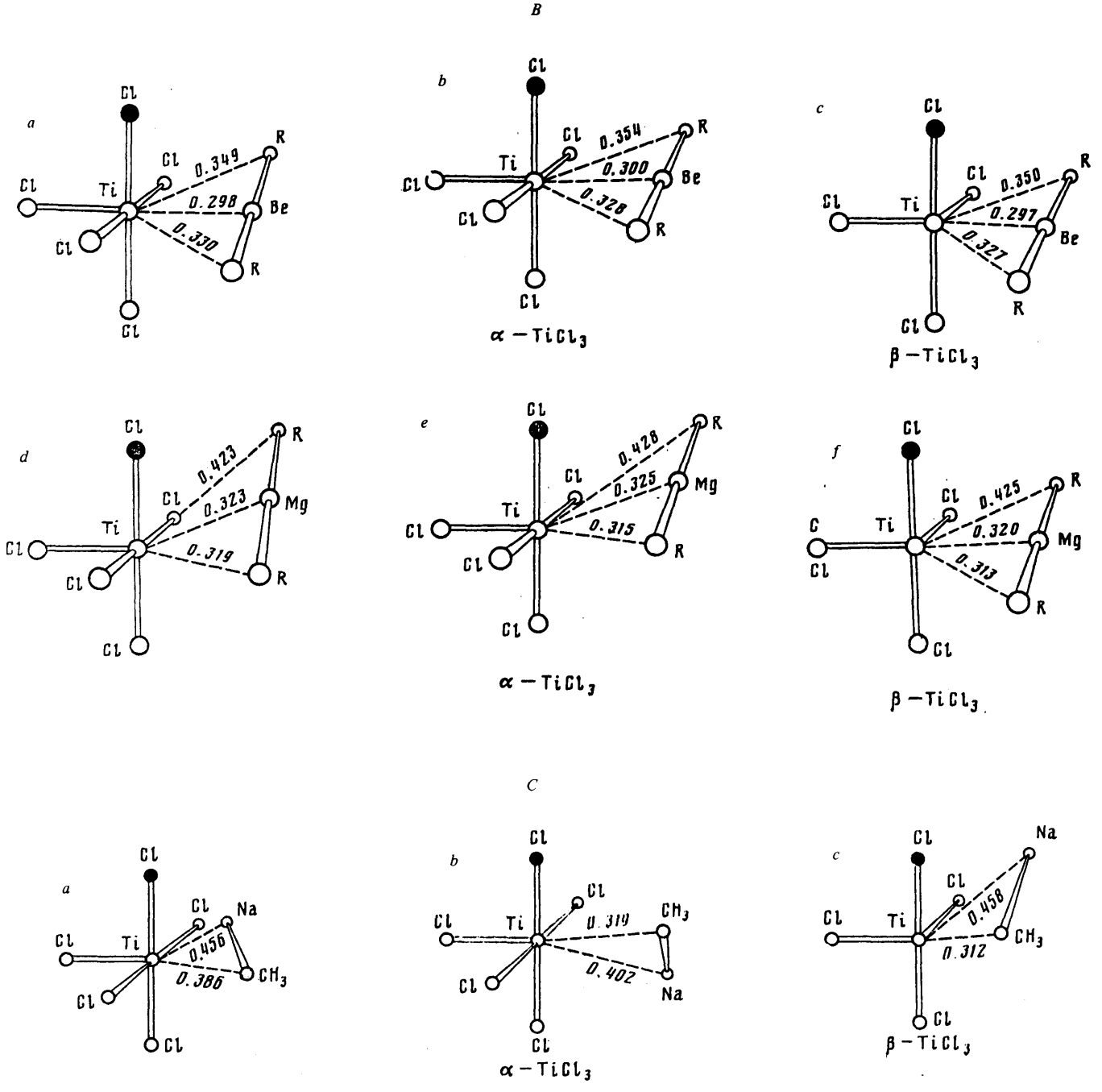



Figure 2 (contd.).

*cis*-poly-1,4-dienes (PAC-2), and atactic polyalkenes and poly-1,2(3,4)-dienes (PAC-3) respectively (Table 1).

The use of the Monte Carlo method[90] made it possible, in calculations of the populations of the PAC, to take account of not only the depth of the potential wells of the energy surfaces in the sorption of the OMC on the crystal, but also their form. At the stage of the physical adsorption of $R_nM$ on the surface of the $TiCl_3$ crystals, the quantitative composition of the centres which on chemisorption are transformed into stereospecific AC was determined. The OMC molecule is fairly firmly fixed on the surface of the crystal, preserving a definite orientation. An important feature is that in the physical adsorption of different OMC on the crystal surface of $M'Cl_3$, structures of the PAC-1, PAC-2, and PAC-3 type with similar geometries are formed, that is the stereospecificity of the action of the Ziegler–Natta catalysts is probably established.

The transformation of the physical adsorption centres into AC in the chemisorption and insertion of the monomer into the growing chain has been examined in detail for the system $(CH_3)_2AlCl–TiCl_3(VCl_3)$.[91] The energy of the configuration was determined using a modified "two-atom complex" method, in which the bond index was used to take account of the directed character and saturated character of the bonds (calculation by the CNDO/2 method).

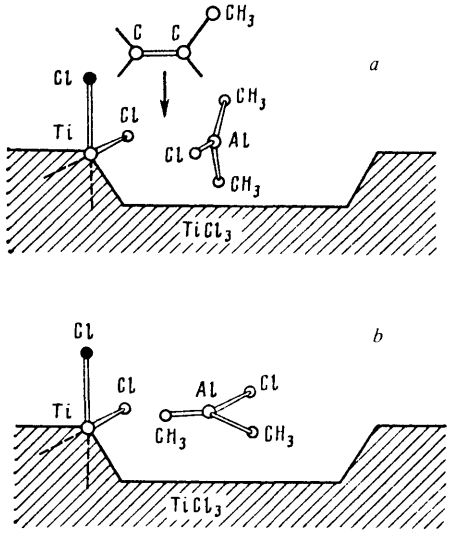



**Figure 3.** Position of the aluminium alkyl on the surface of the $TiCl_3$ crystal (physical adsorption stage): *a*) PAC-1, *b*) PAC-3

**Table 1.** Proportions of different AC and the yield of polymeric stereo-isomeric products in Ziegler–Natta catalytic systems.[42,87–91]

| Catalytic system | Proportions of the AC, % | | | Yield of stereo-isomers*, % (experiment) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CAC-1 (PAC-1) | CAC-2 (PAC-2) | CAC-3 (PAC-3) | poly-propylene | polystyrene | poly-3-methyl-but-1-ene | 1,4-*trans*-PBD | 1,4-*cis*-PBD | 1,2-PBD | 1,4-*trans*-PI** | 1,4-*cis*-PI | 3,4-PI |
| α-$TiCl_3$ + $AlR_3$ | 80 | — | 20 | 75—95 | 90 | 80.4 | 80 | 12 | 8 | 95—100 | — | — |
| γ-$TiCl_3$ + $AlR_3$ | 80 | — | 20 | 80 | — | — | 92 | 8 | — | — | — | — |
| δ-$TiCl_3$ + $AlR_3$ | 80 | — | 20 | 83 | — | — | — | — | — | — | — | — |
| $VCl_3$ + $AlR_3$ | 80 | — | 20 | 73 | 68 | — | 99 | 1 | — | 100 | — | — |
| $CrCl_2$ + $AlR_3$ | 45 | — | 55 | 36 | — | — | 60 | — | 40 | — | — | — |
| $TiCl_2$ + $AlEt_2$ | 98 | — | 2 | 80—90 | — | — | 95.4 | — | 5.5 | — | — | — |
| α-$TiCl_3$ + $BeR_2$ | 92 | — | 8 | 94—97 | — | — | — | — | — | — | — | — |
| α-$TiCl_3$ + LiR | 60 | — | 40 | 10—90 | — | — | 70 | 3 | 27 | — | — | — |
| α-$TiCl_3$ + $MgR_2$ | 75 | — | 25 | 78—85 | — | — | 88 | — | 12 | — | — | — |
| α-$TiCl_3$ + $ZnR_2$ | 0 | 0 | 100 | 30—40 | — | — | 27 | 6 | 67 | — | — | — |
| β-$TiCl_3$ + $AlR_3$ | 60 | 30 | 10 | 40—50 | — | — | 66 | 29 | 5 | 15 | 85 | — |
| α-$TiCl_3$ + NaR | 0 | 0 | 100 | 0 | — | — | 27 | 10 | 63 | — | — | — |
| $CoCl_2$($NiCl_2$, $FeCl_2$) + $AlR_3$ | 20 | 65 | 15 | 20 | — | — | 10 | 74 | 16 | — | — | — |
| β-$TiCl_3$ + $AlRCl_2$ | 100 | — | — | — | — | — | 100 | — | — | — | — | — |

*Isotactic polyalkenes; **PI = polyisoprene.

In the formation of the AC in a system of the type $M'Cl_n \cdot R_mMCl_{3-m}$, the initial stage is the formation of a bridging bond between Ti and Al;[91] the OMC completes the crystal lattice, forming a U' centre similar to that previously described in Refs.11 and 18; the Al atom occupies a position equivalent to the position of Ti; and the alkyl group R occupies a position close to the position of Cl in the layer crystals of $TiCl_3$ (the two-metal AC model). The most important feature of the AC formed (CAC-1, Fig.4*a*) is the formation, with the participation of the R group of the OMC and the M' and M atoms, of a three-dimensional "tent" structure, which plays an important role in the orientation of the monomer in the stereospecific polymerisation process. The AC geometry obtained from the calculations differs little from that proposed in Ref.86 for the two-metal Ti–Al AC model. In the presence of β-$TiCl_3$ and the OMC, in addition to CAC-1, appreciable quantities of other centres, in particular CAC-2 (Fig.4*b*), are also formed on the crystal surface. Their structure in many respects is similar to that of CAC-1, but an important difference is that the Ti atoms react with two R groups (two bridging bonds are formed between the M' and M atoms), so that a different AC coordination sphere is produced, which sterically resembles a "flower" and which is also responsible for the specific orientation of the corresponding monomers in ionic–coordination polymerisation on Ziegler–Natta catalysts.

Thus the combined approach using different methods of study has apparently made it possible: a) to determine clearly the dynamics of formation of the AC while avoiding the main unsatisfactory feature of practically all studies in this field, namely the hypothetical nature of the choice of the AC model; and b) to determine the structure of the polymerisation AC formed on the crystal faces and to show with a much higher probability that the AC of Ziegler–Natta catalysts have a two-metal structure (both components of the catalyst determine the structure of the AC and the mechanism of polymerisation).

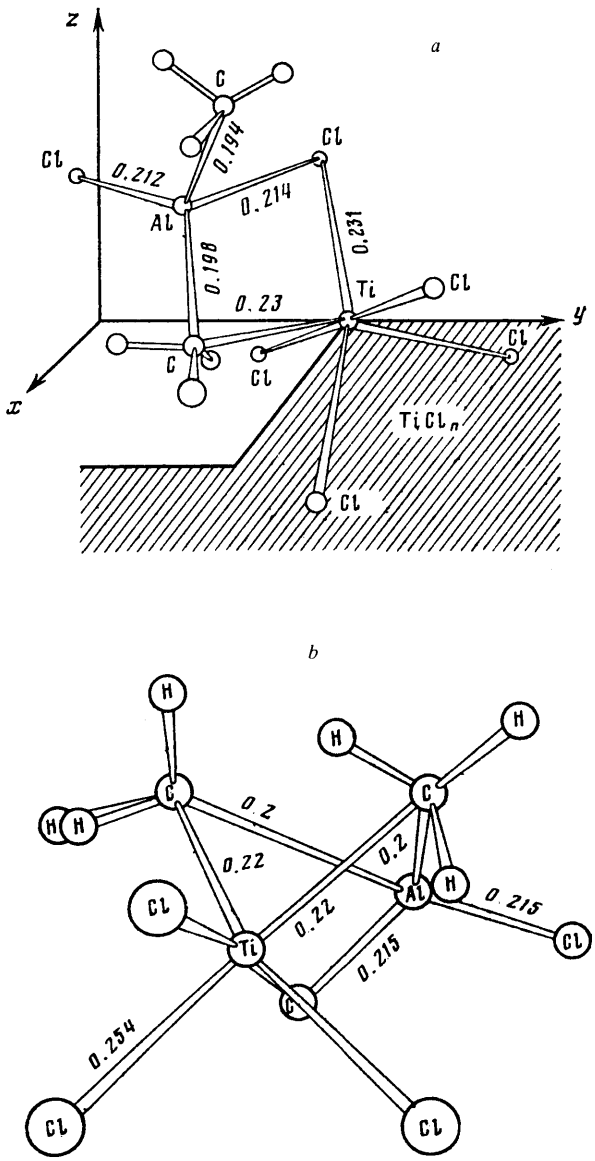



**Figure 4.** Geometry of the model active centre for the catalytic systems (distances given in nm): *a*) α-$TiCl_3$–$Al(CH_3)_2Cl$ (CAC-1); *b*) β-$TiCl_3$–$Al(CH_3)_2Cl$ (CAC-2).

## III. MECHANISM OF STEREOREGULATION

### 1. Empirical Theories

In the polymerisation of α-alkenes and 1,3-dienes under the influence of Ziegler–Natta catalysts, polymers with different micro-structures are obtained, depending on the nature of the components $M'X_n$ and $MR_m$ selected (Table 1). However, although the nature of the AC and the mechanism of the process in the first 10–20 years after its discovery were the subject of a large number of experimental and theoretical studies, the authors of published papers preferred at best to restrict themselves to general phrases about the mechanism of stereoregulation. The existing opinions were essentially probabilistic. Before 1960, no special consideration was given to the question of stereoregulation in polymerisation on Ziegler–Natta catalysts. Since 1960, increasing attention has been paid to this question, and published papers have been specially devoted to the study (including studies by essentially new methods) and interpretation of the surprising property of Ziegler–Natta catalytic systems, namely their ability to give stereoregular polymers based on α-alkenes and dienes with a high steric purity.

#### *a) Mechanism of the Stereoregulation of α-Alkenes*

*The single-metal model of the active centre.* In one of the first papers[6] it was assumed that the stereospecificity of action of the $TiCl_3$–$(C_2H_5)_3Al$ system is due to electrostatic factors. The monomer, situated between the positively charged and negatively charged ions of the catalytic complex, occupies a rigorously definite spatial position.

Cossee and Arlman[33,34,63] assumed that the octahedral $RTiCl_4$ group is positioned unsymmetrically (does not have a plane of symmetry), and that the positions of the R group and the coordination vacancy in the lattice are non-equivalent, from both the steric viewpoint and the viewpoint of

ionic character. This situation predetermines the configuration of the asymmetric carbon atom, that is it allows only one orientation of the coordinated alkene molecule, and this explains the stereospecificity of the action of Ziegler–Natta catalysis.

There are two possible reaction paths: a) after rearrangement, the R group remains in the new position, the monomer is coordinated in the newly formed vacancy, and the whole process is repeated, leading to the alternate participation of the anion vacancy in the acts of chain growth and to the formation of a syndiotactic polymer; b) the longer R group returns to the original position before the introduction of the next monomer molecule. This leads to the repeated introduction of each successive monomer unit into the chain with the preservation of a stereospecifically identical position. In particular, an isotactic polymer is formed in this way. The preference for the isotactic or syndiotactic configuration is determined by the ratio of the rates of the return of the R group to the original position and the introduction of the monomer into the growing chain.

In Ref.98, the migration of the growing MA is not regarded as essential. It is assumed that the insertion of the monomer at the M–C bond takes place without coordination. This suggestion does not appear convincing, however.

In Refs.99 and 100 it was suggested that the stereospecific control is determined by steric factors, namely the reaction of the alkene with the growing chain and the nearest M′ atom.

According to Regs.49 and 101, there are two types of AC on the surface of $(C_2H_5)_3Al[(C_2H_5)AlCl]–TiCl_3$ systems: a) stable AC on which isotactic polymers are formed; and b) unstable AC, which give atactic polyalkenes. The ratio of the centres determines the micro-structure of the MA formed.

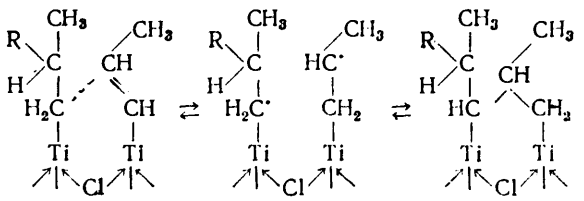
*The two-metal model of the active centre.* As suggested in Ref.5, the formation of macro-chains with the isotactic configuration of the pseudo-symmetrical carbon atom on a heterogeneous AC is due to the asymmetric character of the assumed two-metal AC. Complex formation by the AC and the alkene takes place with opening of the π-bond of the monomer and the production of *d*- and *l*-configurations, depending on the structure of the AC.

According to Ref.7, the stereospecificity of action of Ziegler–Natta catalysts is determined only by the structure of the monomer, whereas according to Ref.52 it depends only on the quantity of $Ti^{2+}$ ions involved in the polymerisation. Isotactic polyalkenes and poly-1,2-dienes, and also *cis*-poly-1,4-dienes, are formed on isolated $Ti^{2+}$ ions. Syndiotactic polymers and *trans*-poly-1,4-dienes are formed with the simultaneous participation of two $Ti^{2+}$ ions.

In Ref.8 it is stated that the stereospecificity of the MA is determined when the monomer is coordinated, as a result of its orientation by the ions of the catalytic complex fixed on the surface of the heterogeneous catalyst (that is by electrostatic factors). The monomer then enters the anionic complex. The existence of hydrogen bonds between the methyl groups and the most electronegative atoms (chlorine) in the complex prevents the free rotation of the growing MA chain.

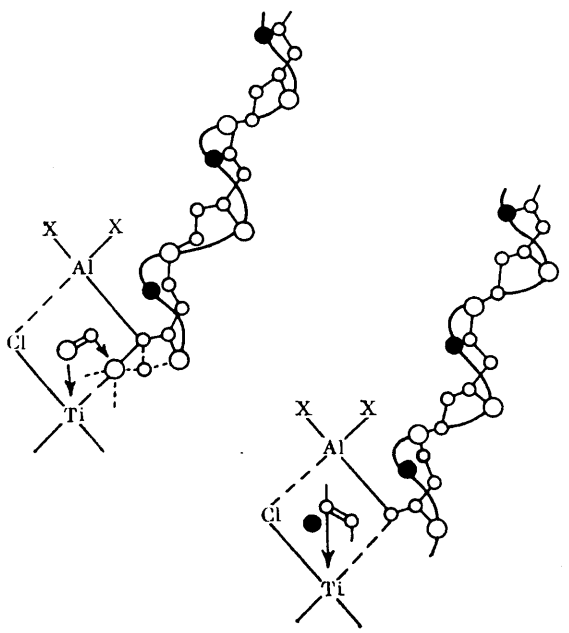
A similar viewpoint was put forward in Refs.10, 13, etc. According to Ref.13, the growing MA moves along breaks in the layers of the $TiCl_2$ and $TiCl_3$ crystals.

In Ref.12 it was assumed that a six-membered complex is formed in the transition state; the OMC serves only to form the initial active M–C bond, which takes no further part in the process:



The presence of hydrogen bonds between successive monomeric units of the growing MA and the AC predetermines the stereospecificity of the growth reaction.

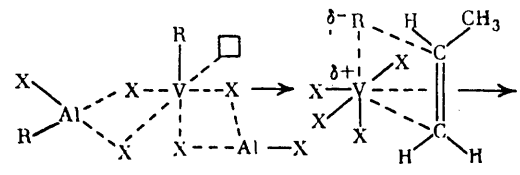
According to Ref.102, the growing MA is a spiral, and the rate of the addition ensuring the symmetry of the spiral is greater than that of any other addition, so that an isotactic polymer is formed from α-alkenes.



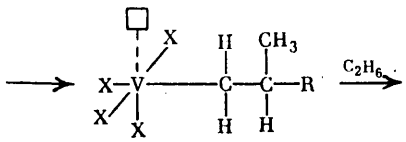
In Ref.59, the stereospecificity of Ziegler–Natta catalysts was attributed to steric factors. In the opinion of the authors cited, the monomer forms a complex with an alkylated octahedral M′(Ti) atom, situated on the lateral faces and defects of an $M'X_n$ crystal with two vacancies, by only the one most probable method, in such a way that the R substituent is directed away from the R groups on the M(Al) atom.

In Ref.103, a scheme for the formation of syndiotactic and atactic polyalkenes was proposed, for the case of the

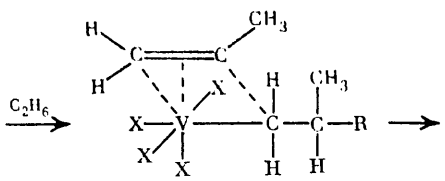
homogeneous $VCl_4$–$(C_2H_5)_2AlCl$ system:



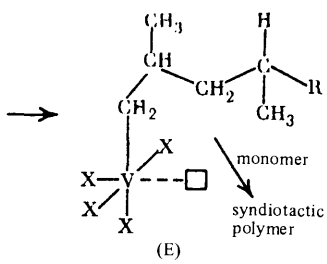
(A) (B)



(C)



(D)




(E)

It is assumed that: a) the coordination of the monomer leading to "head to tail" addition is energetically most favourable; b) the orientation of the $CH_3$ group in the monomer chain, which leads to syndiotactic addition as a result of methyl–methyl interactions, is more favourable than the orientation leading to isotactic addition; c) rotation about the R–M' bond is hindered by steric factors; d) when the barrier to rotation is overcome, for example by increasing the temperature or by using M'(V) complexes with small ligands, the preference for any one orientation of the $CH_3$ group of the entering monomer disappears, so that an atactic polymer is formed.

Thus in all the papers examined above, the stereospecificity of action of Zielger–Natta catalysts is attributed to steric and (or) electrostatic factors, but no clear details of the process are given.

It seems obvious that for the same catalysts, the mechanism of stereoregulation in ionic–coordination polymerisation should be the same for α-alkenes and 1,3-dienes. Stereoregularity in the case of dienes, however, assumes the possibility of not only the isotactic and syndiotactic construction of the MA (1,2- or 3,4-) but also *cis*-, *trans*-, and other forms of isomerism (Table 1). Thus for the polymerisation of dienes, many workers have proposed specific mechanisms relating only to these compounds.

*b) Mechanims of the Stereoregulation of Dienes*

*Single-metal models.* Arlman,[34] using Cossee's model, related the formation of 1,4-*trans*- or 1,4-*cis*-structures to unidentate or bidentate coordination of the monomer to the AC, determined by the accessible space around the M' ion. Unidentate coordination of the monomer leads to the formation of 1,2-, 3,4-, or 1,4-*trans*-units, and bidentate coordination gives 1,4-*cis*-units. A similar view was put forward in Ref. 104. The probability of a given type of coordination is determined by the electronic structure of the M' atom. 1,4-*cis*-Polydienes are obtained when the energy levels of the bonding orbitals of M' and the highest occupied MO of the monomer are close together; when the energy levels differ considerably, polymers with the 1,2- or 1,4-*trans*-structures are formed. The electronegativity of the ligands, which influences the position of the energy levels of the MO of the transition metal, is an important factor in stereoregulation. A similar approach to the examination of the mechanism of stereoregulation was used in Refs. 105 and 106.

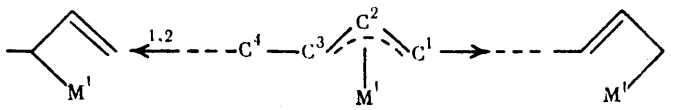
In detailed papers by Dolgoplosk and co-workers,[36–38] the stereoregularity of the MA is related not to the type of coordination of the monomer to the AC but to the configuration of the π-alkenyl unit of the growing MA. At the coordination stage, the diene almost always acts as a bidentate ligand. The introduction of the diene into the chain leads to the formation of a π-allyl complex in the *anti*-conformation. The ratio of the *cis*–*trans* units in the MA is determined by the ratio of the rates of the growth of the chain and the *anti*–*syn*(*cis*-*trans*)-isomerisation of the terminal unit in the AC (scheme 2).

Electron-donor solvating agents, which shield M', increase the lifetime of the terminal unit in the AC, and hence the proportion of *anti*–*syn*-isomerisation. On an AC having only one anion vacancy, dienes are chemisorbed through one double bond (unidentate) in the transoid conformation and enter the chain with the formation of a *syn*-unit (scheme 3). According to scheme 2, reaction (1) leads to the formation of a *cis*-unit, and reaction (2) (isomerisation) to the formation of a *trans*-unit. If the rate of growth is much greater than the rate of isomerisation, the system correspondingly forms chiefly 1,4-*cis*-polydienes.

NMR studies of π-crotylnickel iodide and π-allylnickel fluoroacetate[43,107] showed that the growing terminal group has the *syn*-π-allyl configuration, irrespective of whether *cis*- or *trans*-polymerisation takes place. Thus the 1,4-*cis*- or 1,4-*trans*-polymerisation of dienes can be explained[107] by the intramolecular coordination (*syn*–*anti*) of the double bond situated next to the π-allyl bond at the end of the MA. In this case the *syn*-form, as in the theory of Dolgoplosk,[36–38] favours *trans*-polymerisation, whereas the *anti*-form favours the *cis*-polymerisation of the dienes. At the same time it should be borne in mind that the coordination of the penultimate double bonds of the growing polybutadiene chain is most probably excluded.[106]

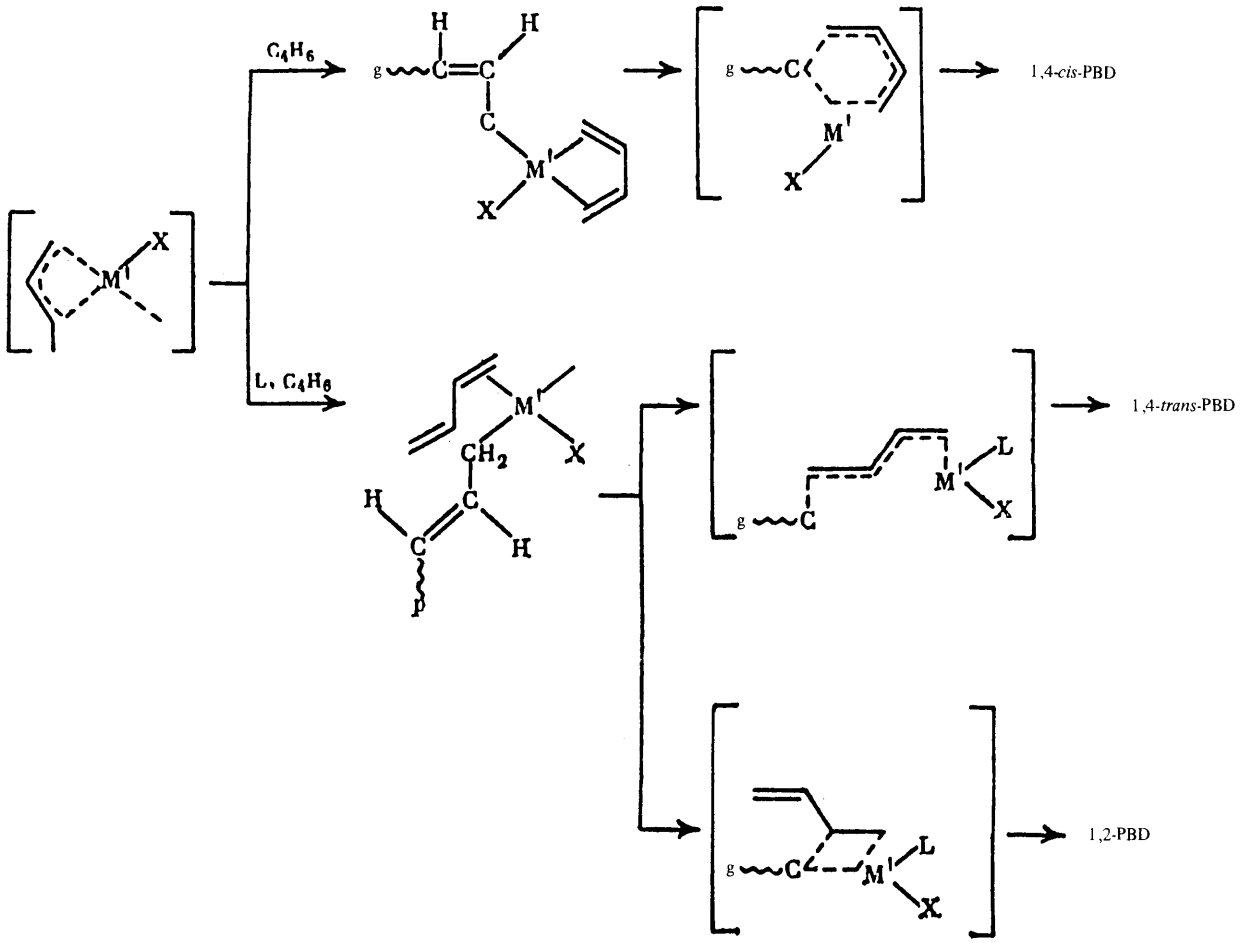
The concept of π-allyl control of stereospecificity is also supported by other authors.[108] In their opinion, in the polymerisation of dienes a π-allyl bond is formed between the M' atom and the last unit of the growing MA. The π-allyl unit contains two reactive atoms, C(1) and C(3). The reaction of the sorbed monomer with C(1) leads to the production of 1,4-*trans*- or 1,4-*cis*-polymers (depending on whether the structure of the allyl group is *syn* or *anti*),

whereas the reaction with C(3) gives 1,2-structures:

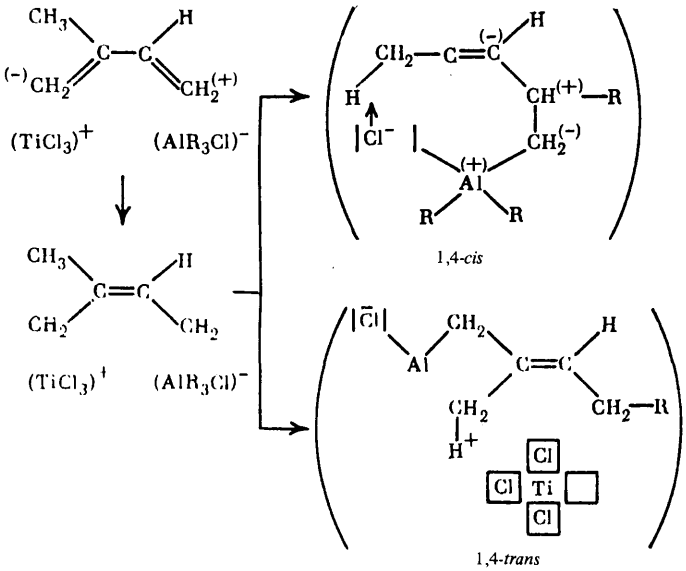


Here, the sorbed monomer reacts with the less extensively substituted and hence more reactive carbon atom. In a later paper by the same authors[109] it is also stated that the formation of 1,4-*trans*-polymers depends on the type of catalyst and may take place either with the coordination of only one C=C double bond to the AC, or with the coordination with the monomer through two double bonds with the formation of an *anti*-butenyl group and subsequent *anti–syn*-isomerisation. According to Ref.109, the formation of isotactic (*erythro*-di-isotactic) and syndiotactic (*threo*-disyndiotactic) polydienes is determined by the reaction of the monomer molecules with the ligand environment or with the butenyl group of the AC.

Various authors have tried to summarise the available experimental results and schemes for the mechanism of the stereospecific polymerisation of dienes. In particular, in Ref.43 the mechanism of formation of stereoregular polybutadienes (PBD) in solution is represented by the scheme:



*Two-metal models.* According to Ref.8, the polymerisation of dienes takes place on ionic complexes $(TiCl_3)^+(AlR_3Cl)^-$, like the polymerisation of α-alkenes. The chief factor determining *cis*- or *trans*-addition is the geometric configuration of the monomers.




This hypothesis does not explain many familiar experimental facts, in particular why 1,4-*trans*-polydienes are mainly formed in the presence of α-$TiCl_3$, and 1,4-*cis*- and 1,4-*trans*-polydienes on β-$TiCl_3$.[41-49]

In Ref.110 it is considered that the structure of the polymers formed is determined only by the geometric structure of the crystal lattice of the heterogeneous component. This hypothesis, however, applies only to the polymerisation of isoprene on $TiCl_3$, and does not deal with the stereospecificity of action of other catalysts and monomers. It also does not explain the role of the cocatalyst and the influence of various additives on the stereoregulation process.

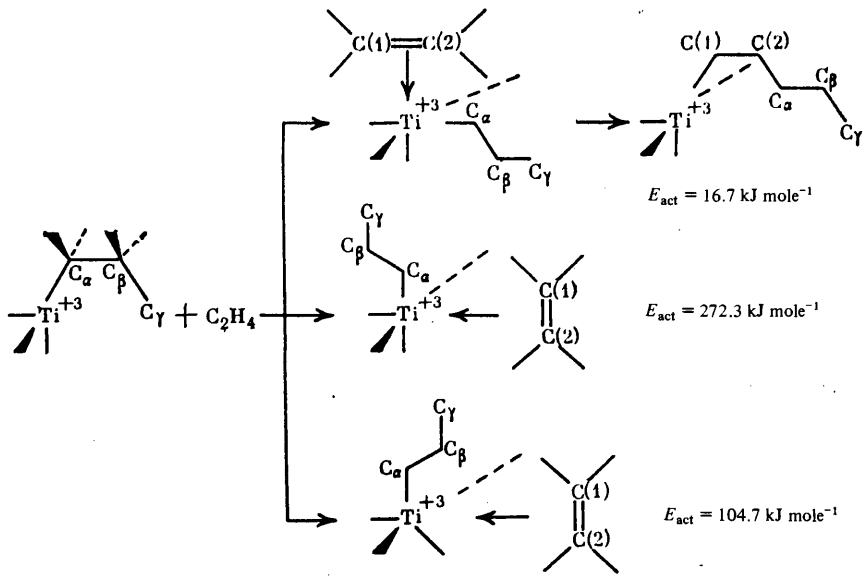
Thus to explain the stereospecific action of Ziegler catalysts for the polymerisation of dienes, research workers have introduced not only electrostatic but also steric factors and various data on the structure of the monomers (polymers).

Two main views regarding the mechanism of stereoregulation in the polymerisation of dienes in the presence of Ziegler–Natta catalysts are widely discussed in the literature: a) the theory of *cis–trans* geometric control, which takes account of the presence of two C=C bonds in the conjugated dienes and hence the possible coordination of the diene through one or two double bonds to the AC (unidentate and bidentate coordination); and b) the theory that the configuration of the polymers is determined by the π-alkenyl polymer–M′ bond (the *anti*-form facilitates the formation of *cis*-units). The schemes put forward, however, do not provide a convincing interpretation of many available experimental data, for example the influence of the nature of M′ on the stereospecificity of action of Ziegler–Natta catalysts, etc.

## 2. Present-day Trends

### *a) Mechanism of the Stereoregulation of α-Alkenes*

Detailed studies of the mechanism of stereoregulation in polymerisation on Ziegler–Natta catalysts using quantum-chemical methods were begun comparatively recently, and only a few have as yet been published. Two series of studies are noteworthy. In one series[81-85] it was shown that there are three possible paths for the introduction of the monomer into the coordination sphere of M′ in AC with the *cis*-structure of the growing MA.



The smallest $E_{act}$ corresponds to the introduction of the monomer on $C_\alpha$ side, after which *cis–trans*-isomerisation is possible. The energetic non-equivalence of the different paths for the introduction of the monomer into the AC with the *cis*-configuration of the growing MA eliminates the need for the migration of the R group from one octahedral position to another, as in the Cossee mechanism. The active centre with the *cis*-MA leads to the formation of isotactic polymers, and that with the *trans*-MA to the formation of atactic polymers. The probability of the *cis–trans*-isomerisation of the R group of the AC, however, depends on the structure of the surface of the Ziegler–Natta catalyst and the presence of various adsorbed reagents in the immediate environment.

In Refs.111 and 112 the Cossee model was used to estimate the energy of the non-bonding interactions in the coordination of the monomer with the AC on the surface of the crystal for different cases of diastereo-isomerism, and it was concluded that the stereospecificity of Ziegler–Natta catalysts is due to the chirality of the ligand environment of the catalytically active Ti atom. The latter determines the orientation of the first C–C bond of the chain, which influences the subsequent mode of insertion of the monomer. In the case of the alkylation of Ti chlorides by trimethylaluminium, however, the system is not stereospecific with respect to the polymerisation of alkenes. An obvious meritorious feature of these studies is that, as in Refs.87–92, account was taken of the real surface of the heterogeneous component.

*b) The Mechanism of the Stereoregulation of 1,3-Dienes*

In Ref.113, from an analysis of the MO diagram of the active catalyst–monomer complex, it was suggested that the microstructure of polybutadiene is determined by the mode of coordination of the monomer (bidentate or unidentate), and depends on the electron density at the M′ atom. The probability of coordination of a given type is determined by the difference in the energy levels of the bonding molecular orbitals of M′, which accepts electrons from butadiene, and the highest occupied MO of butadiene. When these levels are close together, 1,4-*cis*-polydienes are obtained; when they differ considerably, polymers with 1,2- or 1,4-*trans*-structures are formed. The electronegativity of the ligands, which influences the position of the energy levels of M′, obviously also influences the stereospecificity of action of Ziegler–Natta catalysts.

Thus the quantum-chemical study of stereoregulation has apparently not made it possible to extend significantly the empirical theories and has only confirmed that the stereospecificity of action of Ziegler–Natta catalytic systems is due to both steric and electrostatic factors.

## 3. Recent Progress

In Refs.87–92 it has been clearly shown that the stereospecificity of action of Ziegler–Natta catalysts is determined by the three-dimensional structure of the coordination sphere of the AC and by the chemical character of the monomer, and it has been shown that the nature and mechanism of stereoregulation are the same for the polymerisation of α-alkenes and dienes.

*a) Polymerisation of α-Alkenes*

Stereoregulation in the polymerisation of α-alkenes is determined by the geometric structure of the AC.[87–90] The use of α-$TiCl_3$–$R_2AlCl$ on a titanium trichloride surface leads to the formation of one of the most frequently encountered OMC configuration with an energy $E_1 = -127.61$ kJ mole$^{-1}$ and $F_1 = 38\%$ ($F_i$ is the fraction of the individual configuration with energy $E_i$ in the total balance of the PAC; $i = 1$, 2, 3, etc.), and also configurations with similar structures with $E_2 = -126.78$ kJ mole$^{-1}$, $F_2 = 27\%$ and $E_3 = -125.1$ kJ mole$^{-1}$, $F_3 = 14\%$ (*a–c* in Fig.2*A*). The last two configurations differ from the first only in the "interchange" of the Cl atom and the $CH_3$ group, while the position of the Al atom remains unchanged. The total contribution of these configurations is about 80%.

For β-$TiCl_3$ a large number of different versions of the arrangement of $R_2AlCl$ on the crystal surface has been found, but in this case also it is possible to distinguish three most favourable configurations with energies of −120, −124.68, and −119.9 kJ mole$^{-1}$ (*d–f* in Fig.2*A*). The total contribution of these configurations is much smaller than in the case of α-$TiCl_3$, and amounts to 30%; as in the case of α-$TiCl_3$, these configurations differ only in the interchange of the Cl atom and the $CH_3$ group while the position of the Al atom remains unchanged. Moreover, it has been found that the geometry of the PAC has much in common for the different forms (α and β) of $TiCl_3$. In both cases there is a good correspondence between the yield of stereoregular polymers of alkenes and the proportions of PAC-1. The only difference between the α- and β-forms of $TiCl_3$, which have hexagonal close-packed Cl atoms, but which differ in the positions of the Ti atoms, is that when α-$TiCl_3$ is used the quantity of PAC-1 formed is approximately 80% of the total (Fig.2*A* and Table 1), and the MA obtained are correspondingly highly isotactic, whereas when β-$TiCl_3$ is used the proportion of these PAC is only 30%.

An important feature is that PAC with similar structures (Fig.2*B*) are also formed in the systems $R_2Be$–α-$TiCl_3$ ($F = 94\%$), $R_2Be$–β-$TiCl_3$ ($F = 50\%$), $R_2Mg$–α-$TiCl_3$ ($F = 75\%$), and $R_2Mg$–β-$TiCl_3$ ($F = 20\%$),[89,90] etc. Here also there is good agreement between the yield of isotactic polyalkenes and the PAC-1 population (Table 1).

The geometries of PAC of the same type formed on the surface of α-$TiCl_3$ and β-$TiCl_3$ in combination with different OMC are practically identical (Fig.2).

The chief difference between the PAC-1 configurations distinguished and other configurations formed as a result of the sorption of OMC on the crystals is the unique position on the $TiCl_3$ surface of the weakly bound Cl and Ti atoms and the M and Cl atoms and R groups of the OMC molecule, as a result of which, when the monomer molecule approaches, the C=C bond may be attacked simultaneously by both the Ti atom and the RA1< fragment (Fig.3). The "push–pull" mechanism corresponds to the concept of the two-metal catalysis[11,18] of the polymerisation of α-alkenes (schemes 4 and 5). A propene molecule on the crystal surface is probably fixed only in one position in which the $CH_3$ group of propylene is directed away from the surface, leading to an isotactic sequence in the addition of the monomeric units of the MA in the polymerisation of propene on Ziegler–Natta catalysts.

A similar process is characteristic of the specific PAC of the same type formed by the combination of various OMC with the α- or β-forms of $TiCl_3$, $VCl_3$, etc., and is not observed on other PAC (for example those formed by the reaction of $TiCl_3$ with RNa or $R_2Zn$), whose structures differ from that of the centres given in Fig.3*a*. An example is the

configuration with $E = -119.66$ kJ mole$^{-1}$ ($S = 3\%$) on the surface of $\alpha$-$TiCl_3$ (Fig.3*b*). In this case the OAC molecule is coplanar with the crystal surface, and a specific arrangement of the atoms, as in PAC-1, is not observed. A propene molecule may be fixed on an AC of this type in several positions, leading to non-stereoregular polymerisation.

Additional confirmation that the PAC-1 are responsible for the production of isotactic polyalkenes is provided by the fact that with increase in temperature from 300 K to 330 K, according to calculations for $R_2AlCl$–$TiCl_3$ systems, the proportion of stereoregular AC of the same type decreases by an average of 5% (the value at 330 K is 75% and 25% for $\alpha$- and $\beta$-$TiCl_3$ respectively[87]). This agrees with experimental data on the yield of isotactic polypropylene in the polymerisation of the monomer.[114] In accordance with experiment[41,42] and calculations,[87,88] on going from the solid surface to the catalyst solution, the appearance of the corresponding energy spectrum in the reaction of $M'Cl_n$ with the OMC becomes impossible, and the formation of stereoregular polymers of $\alpha$-alkenes is excluded.

The calculation for systems containing NaR [89] showed three configurations: one on $\alpha$-$TiCl_3$ with an energy of $-135.14$ kJ mole$^{-1}$, and two on $\beta$-$TiCl_3$, with energies of $-117.83$ kJ mole$^{-1}$ (Ti atom with one vacancy) and $-114.65$ kJ mole$^{-1}$ (Ti atoms with two vacancies) (Fig.2*C*). This system does not contain centres whose structure might be similar to PAC-1 when the $\alpha$- and $\beta$-forms of $TiCl_3$ are used (Figs.2*A* and 2*B*), as in the previous systems. The arrangement of NaR on the surface of the $TiCl_3$ crystal is similar to the arrangement of the OAC in a non-stereospecific centre, in which one of the R groups is closer to the Ti atom than the Al atom. Polymerisation in the $TiCl_3$–RNa system takes place as on the non-stereospecific (for $\alpha$-alkenes) centres PAC-3 in $TiCl_3$–OMC systems (Fig.3*b*). The difference between these catalytic systems is revealed by the fact that in the presence of NaR all the centres are non-stereospecific for the polymerisation of $\alpha$-alkenes, whereas in the other systems involving OMC, non-stereospecific AC make up only a fraction of the total number. Thus for each system there are several types of PAC, and stereospecific PAC are encountered in catalysts containing both $\alpha$-$TiCl_3(VCl_3)$ and $\beta$-$TiCl_3$. The calculated proportions of stereospecific centres in the above series of systems correlates with the experimental yields of isotactic polypropylene and other polyalkenes (Table 1).

The stereospecificity of the AC depends both on the nature of the OMC and on the nature of the arrangement of the OMC on the surface of the $M'X_n$ crystal. In catalysts containing compounds of metals of the first group, there are practically no stereospecific PAC either in brown $\beta$-$TiCl_3$ or in the violet $\alpha$- and $\gamma$-forms of $TiCl_3$. In heterogeneous catalysts based on $TiCl_3$ and OMC of the metals of the second and third groups, stereospecific AC are mainly formed, and their concentration is appreciably greater in the systems with the $\alpha$-, $\gamma$-, and $\delta$-forms of the $TiCl_3$ crystal, correlating with the yield of isotactic polyalkenes.

*b) Polymerisation of Dienes*

The formation of specific polymerisation centres of the same type, determining the stereo-isomerism of the macromolecules, when MOC are adsorbed on an $M'Cl_n$ surface is a general phenomenon for processes involving both polyalkenes and polydienes.

A strict correlation is observed between the yield of 1,4-*trans*- and 1,4-*cis*-polydienes in the polymerisation of dienes in the presence of different forms of $TiCl_3$ and OMC and the proportions of PAC-1 (CAC-1) and PAC-2 (CAC-2) respectively (Table 1)¶. An interesting feature is that calculations carried out for catalysts based on $\alpha$-($\gamma$-)$TiCl_3$–OMC and $CrCl_3$–OMC revealed differences in the nature of the change in the proportions of 1,4-*trans*- and 1,2-polydienes with change in the temperature of preparation of the catalyst. The results of the calculations were confirmed experimentally (Table 2). On the CAC-1 ("tent") in the polymerisation of dienes, the formation of 1,4-*trans*-units is energetically favourable, and in the process of chain growth there is no hindrance to the physical adsorption of the subsequent monomer molecules (Fig.5).[92] The unidentate coordination and the energetically favourable character of the formation of 1,4-*trans*-polydienes, brought about by the presence of the CAC-1 ("tent"), are responsible for a number of characteristic features of the polymerisation of dienes in the $AlR_3$–$\alpha$-$TiCl_3$ system: the formation of up to 80–90% 1,4-*trans*-polydienes and a correspondingly small proportion of 1,2- and 3,4-structures, and a decrease in the rate of polymerisation of substituted dienes (isoprene, pentadiene, etc.) compared with butadiene, because of the definite steric hindrance to the approach of the molecule to the CAC-1 on the side of the substituent. This effect may also explain the anomalous behaviour of 1,4-diphenylbutadiene and 4-methylpenta-1,3-diene in their polymerisation in the presence of Ziegler–Natta catalysts.[92] 1,4-Diphenylbutadiene is not polymerised for steric reasons, as can be clearly seen from Stuart–Briegleb models. For the same reasons, 4-methylpenta-1,3-diene forms practically only 1,2-poly-4-methylpentadiene.

Table 2. Dependence of the yield of stereo-isomers of polybutadiene on the temperature of the preparation of the catalytic complex in systems involving $CrCl_3$ and $TiCl_3$.

| Catalytic system | $T^*_{prep}$, °C | Proportion of AC, % (calculated) | | Yield of polybutadiene, % | |
|---|---|---|---|---|---|
| | | PAC-1 | PAC-3 | 1,2- | 1,4-*trans* |
| $CrCl_2 + AlR_3$ | 40 | 45.9 | 54.1 | 36.3 | 63.7 |
| | 50 | 46.3 | 53.7 | 39.4 | 60.6 |
| | 60 | 47.1 | 52.9 | 27.8 | 72.2 |
| | 70 | 47.6 | 52.4 | 25.6 | 74.4 |
| | 80 | 48.1 | 51.9 | 24.7 | 75.3 |
| $\gamma$-$TiCl_3$+$AlR_3$ | 40 | 80 | 20 | 10 | 90 |
| | 50 | 79.5 | 20.5 | 7 | 92 |
| | 60 | 79 | 21 | 11 | 87 |
| | 70 | 78.5 | 21.5 | 12 | 86 |
| | 80 | 77 | 23 | 13 | 85 |

*$T_{prep}$ is the temperature of preparation of the catalytic complex.

Note. Al/Cr = 2, [$CrCl_3$ = 0.01 M, [M] = 2.5 M; Al/Ti = 2, [$TiCl_3$] = 0.04 M, [M] = 1 M; polymerisation temperature 50 °C.

On CAC-2, which have an essentially different steric structure ("flower") and which are formed, for example, when $\beta$-$TiCl_3$ is used in combination with $R_3Al$ or $R_2AlCl$, bidentate coordination of the monomers with the formation

———.

¶ The chemical adsorption centres (CAC) are formed at the stage of the chemical adsorption of the OMC on the surface of the heterogeneous component of the catalyst from the corresponding PAC.[91,92]

of 1,4-*cis*-polydienes is energetically favourable, as observed in practice.[115] Growing MA with the 1,4-*cis*-configuration of the units show the least steric hindrance to the approach of the monomer to the catalytically active Ti atom.

A third type of AC (CAC-3, "wicket") (Fig.3*b*), practically indistinguishable from PAC-3 and characterised by a large coordination sphere volume, has been detected. These AC show a weak interaction between the components of the catalytic complex $M'X_n$ and the OMC. Analysis of the experimental data (Table 1) indicates that 1,2(3,4)-polydienes are most probably formed on CAC-3.

Thus CAC-1 are stereospecific in the polymerisation of α-alkenes and dienes, CAC-2 are not stereospecific in the polymerisation of α-alkenes, but give 1,4-*cis*-polydienes,

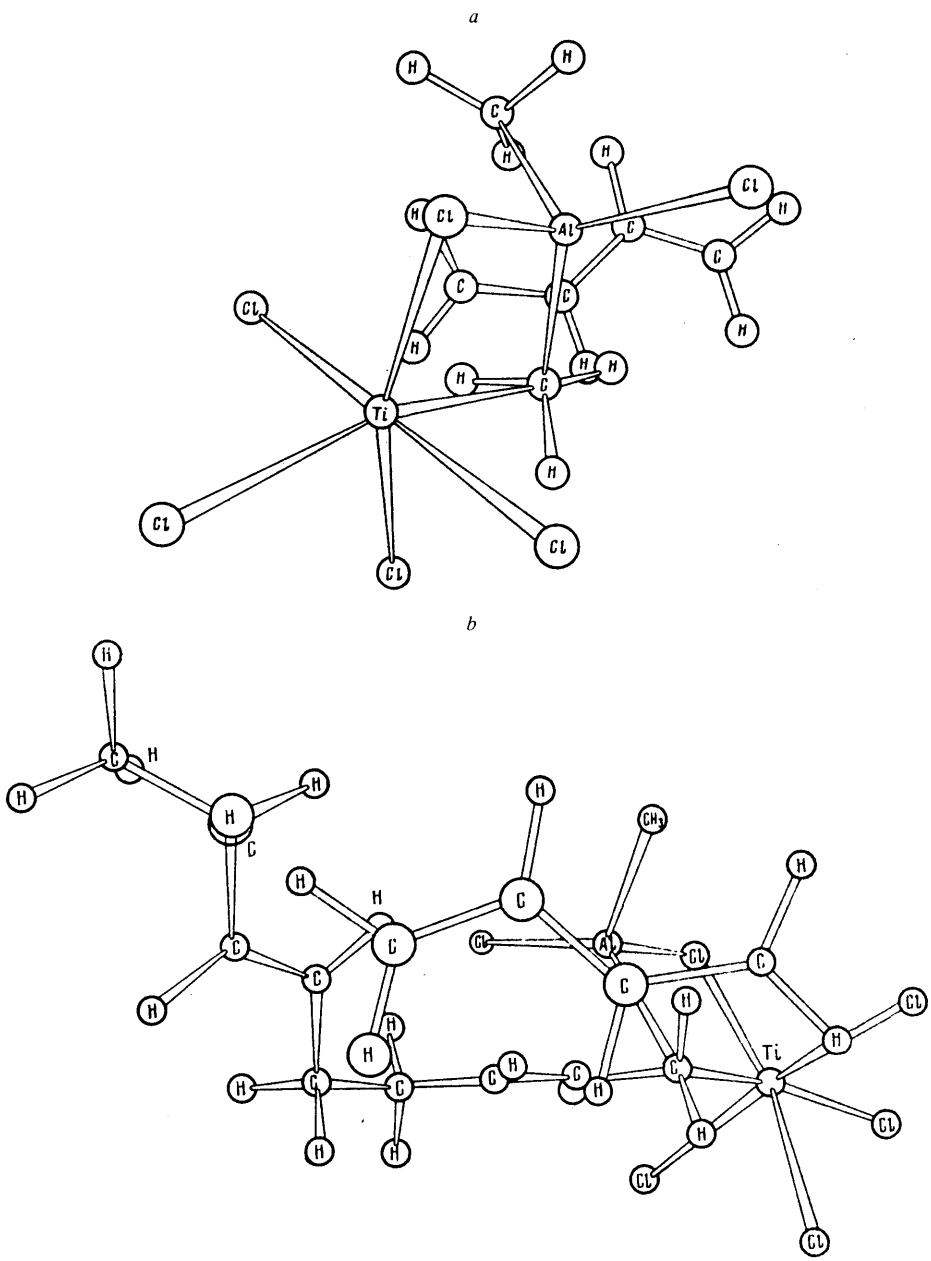



**Figure 5.** *a*) The coordination of butadiene with an active centre (stage of physical adsorption on the AC); *b*) physical adsorption of butadiene on an active centre with a growing 1,4-*trans*-polymer chain.

and CAC-3 bring about the non-stereospecific polymerisation of α-alkenes and dienes with the formation of atactic polyalkenes and 1,2(3,4)-polydienes. A theoretical base has been developed, which makes it possible, without carrying out tedious experimental searches, as has been done up to the present, to select in a first approximation (without allowance for kinetics) new Ziegler–Natta catalysts for the stereospecific polymerisation of α-alkenes and dienes.

## IV. SUMMARY

Since the discovery of stereospecific polymerisation by Ziegler and Natta, a very large number of experimental and theoretical studies of the nature of the AC and the mechanism of stereoregulation have been published.

In the first twenty-year period (1954–75), a large number of hypothetical ideas were put forward, based on a limited amount of experimental material. It was shown that polymerisation on Ziegler–Natta catalysts is an ionic–coordination process in which the AC has a stereoregulating action on the micro-structure of the macromolecules. Two models of the AC, single-metal and two-metal, have been discussed. Although the polymerisation scheme on single-metal AC has been adopted by most workers, there are nevertheless many experimental data which are fundamentally inconsistent with this and similar theories. Polymerisation schemes involving AC with a two-metal structure are much more probable. The stereoregulating action of Ziegler–Natta catalytic systems is due to steric and (or) electrostatic factors.

The use of quantum-chemical calculations essentially has not led to an improvement in existing theories. They have merely confirmed various particular details of the process, or, at best, refined or slightly extended theories of the characteristic features of the electronic structure of AC. This at first sight unexpected result has a quite definite cause, namely the *a priori* selection of the structure of the AC in the quantum-chemical calculation, generally without allowance for the real structure of the $M'X_n$ and the OMC molecules, in accordance with the subjective sympathy of the authors for the single-metal or two-metal model of the AC.

At the same time, the comprehensive approach to the theoretical study and modelling of the process using semi-empirical and empirical methods of calculation and numerical experiment at all stages, from the physical adsorption of the homogeneous organometallic component on the real surface of the heterogeneous component of the Ziegler–Natta catalytic system to the formation of the AC and their participation in the process of polymerisation and stereoregulation, has enriched the theories with new and fruitful ideas, and hence made possible a new approach to the development of the theory of the processes of ionic–coordination stereospecific polymerisation of alkenes and dienes. In particular, the structure of the AC and the dynamics of their formation have been determined, and it has been shown that the stereospecificity of action of Ziegler–Natta catalysts is determined by the structure of the coordination sphere of the catalyst, and that stereoregulation takes place by a single common mechanism in the polymerisation of alkenes and dienes. Three types of adsorption centre differing in their three-dimensional structure have been identified: CAC-1, "tent" (isotactic polyalkenes and 1,4-*trans*-polydienes are formed), CAC-2, "flower" (atactic polyalkenes and 1,4-*cis*-polydienes), and CAC-3, "wicket" (atactic polyalkenes and 1,2(3,4)-polydienes).

Thus the traditional and up to the present the only empirical method for finding new effective Ziegler–Natta catalysts by tedious experimental searches can be replaced by numerical experiments involving the estimation of the proportion of stereoregulating AC determining the stereoisomerism of the MA formed.[87–92]

Naturally, there are a number of unsolved problems, such as the influence of various modifying additives on the rate of polymerisation and the properties of the AC, the detailed mechanism of the excitation of the polymerisation of alkenes and dienes, and the influence of the kinetics of polymerisation on the yield of the stereo-isomers of alkenes and dienes in the presence of specific Ziegler–Natta catalysts and monomers.

Another unresolved problem is the apparently fundamental question of the justification for classifying individual organometallic compounds of transition metals, showing stereospecificity in the polymerisation of dienes and cycloalkenes,[36–38] as Ziegler–Natta catalytic systems. The possible production of stereoregular polydienes in the presence of individual M′ compounds is the main argument used by supporters of the concept of single-metal catalysis. These compounds apparently represent a new generation of organometallic catalysts of the stereospecific polymerisation of dienes and cycloalkenes, and they should not be regarded as classical Ziegler–Natta catalysts. They apparently represent a unique new type of stereospecific catalyst. It is more correct to regard them as a separate class and to call them Dolgoplosk catalysts in honour of the leader of the school which has established priority in the development of the synthesis of individual transition metal OMC and the study of their catalytic activity and the mechanism of stereoregulation in stereospecific polymerisation, the copolymerisation of dienes, and metathesis (Refs.36–38, 62, etc.). This should lead in the near future to the general acceptance of the mechanism of two-centre catalysis in the stereospecific coordination–ionic polymerisation of alkenes and dienes on Ziegler–Natta catalysts. This, together with a deeper understanding of the processes of catalysis and stereoregulation, will provide a basis for the further development of improved methods for the directed control of the stereospecific polymerisation of alkenes and dienes.

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# The Reactions of Nitrile-containing Polymers

E.N.Zil'berman

The present review deals with chemical aspects of the reactions of polyacrylonitrile and related polymers, based on the reaction of the C≡N groups, the polymer-analogue transformations of polynitriles under the influence of water, alcohols, carboxylic acids, nitrogen-containing organic compounds, hydrogen sulphide, and other nucleophilic reagents, and the reaction of polynitriles with electrophilic reagents. Reactions undergone by the polymers but not by mononitriles, and reactions whose mechanisms are different for poly- and mononitriles, have been distinguished. The review cover the literature of the last 15 years. The bibliography contains 143 references.

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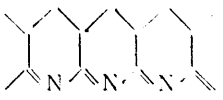
## I. INTRODUCTION

As a consequence of the high and varied reactivity of the cyano-group, the properties of nitrile-containing polymers can be modified comparatively easily by treating these polymers with various reagents. A number of reactions of polynitriles, primarily reactions based on the hydrolysis of polyacrylonitrile (PAN), are widely used in industry. The reactions of nitrile-containing polymers have been reviewed in monographs[1,2] covering the literature for the period 1967–1970. In recent years, however, a large number of studies of fundamental importance have been carried out on the chemical transformations of macromolecular compounds containing nitrile groups. The present review is based mainly on papers published during this period. Of earlier work, only important studies not dealt with in Refs. 1 and 2 have generally been examined. The present review does not deal with work on the intramolecular reactions of the nitrile group with other functional groups to give heterocyclic compounds, since these reactions, which are used, in particular, to obtain heat-resistant polymers ("polyheteroarylenes"), were reviewed recently.[3]

The thermal treatment of polymers containing blocks consisting of nitrile-containing units leads to polymerisation at the CN groups to give polyazomethines (azapolyenes). This polymerisation can take place at the same time as the polymer-analogue reactions of polynitriles, and, as shown below, in a number of cases it precedes other transformations of the macromolecules. The present reivew begins with an examination of the influence of various reagents and functional groups (present in the original polymers or formed during thermal decomposition) on the polymerisation at the CN groups. The review does not examine the many studies of azapolyenes not concerned with the chemical nature of the observed conformations, studies of the thermal decomposition of CN-containing polymers at temperatures above 200–300 °C, or studies of the volatile products formed in the thermal decomposition of nitrile-containing polymers.

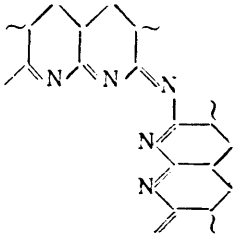
## II. INTRA- AND INTERMOLECULAR REACTIONS OF CN GROUPS

Heating (100–200 °C) polymers rich in acrylonitrile and methacrylonitrile units leads to the intramolecular reaction of neighbouring nitrile groups to give sections with a ladder structure, for example:



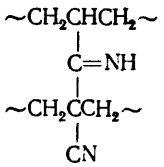
This reaction[1,2,4,5] continues to attract considerable attention, chiefly because it is a basic reaction in the degradation of nitrile fibres, accompanied by discolouration, and also because polymerisation at the CN groups of PAN is the first stage in the production of carbon fibres.

When PAN is heated, the intramolecular transformations are evidently accompanied by intermolecular reactions of the CN groups, leading to cross-linking of the polymer chains:[6,7]



The sections consisting of condensed rings are relatively short. They are formed by not more than 3–5 neighbouring units, and this is apparently related to the atactic structure of PAN.[6,8–11] The intermolecular reaction gives not

only N–C bonds, as shown above, but also C–C bonds:



Structure formation by the macromolecules during polymerisation makes the products insoluble. The ladder polymer based on polymethacrylonitrile (PMAN), after polymerisation at the CN groups, remains soluble in various solvents. This is related to the fact that PMAN does not contain relatively mobile α-hydrogen atoms, which in the case of PAN are responsible for the formation of intermolecular C–C bonds; steric factors also prevent intermolecular interaction.[1] When CN-containing polymers are heated to 200 to 250 °C, other processes accompanying structure formation, namely the rupture of polymer chains and the liberation of volatile degradation products, take place more intensively, and dehydrogenation or oxidative dehydrogenation leads to aromatisation of the condensed rings. The chains are broken much more easily in dimethyl sulphoxide (DMSO) solution than when the solid polymer is heated.[12] The slowest stage in the various successive transformations of PAN and similar polymers, however, is cyclisation, that is the rate of polymerisation at the CN groups determines the overall rate of the process.[13]

The presence of isotactic sequences in the PAN chain creates the most favourable conditions for the formation of polyconjugated systems. Increase in the concentration of these sequences is accompanied by an increase in the length of the conjugation chains in PAN subjected to thermal treatment.[5,14–16] An important part in the kinetics of the transformations of PAN is also played by the conformation of the polymer chain.[5]

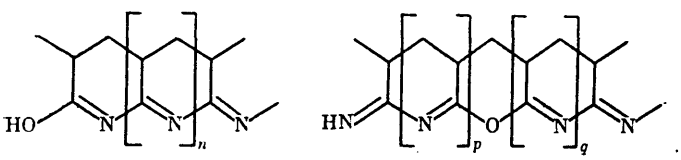
The treatment with nucleophilic reagents of polymers whose macromolecules contain blocks consisting of nitrile-containing units, or the introduction of nucleophilic functional groups into the macromolecules of these polymers, initiates polymerisation at the CN groups. A marked increase in the rate of formation of polycyclic structures in the thermal decomposition of nitrile-containing polymers is achieved in the presence of carboxyl groups.[1,17–26] When substituted acetic acids are added to PAN, intensive polymerisation at the CN group takes place even at 100 °C, and its rate increases with increase in p*K* for the acid. The rate of the process is also increased by hydrogen chloride.[27] The lower initial temperature of cyclisation in copolymers of acrylonitrile and vinylidene chloride, compared with PAN, is apparently due to the action of the hydrogen chloride liberated in the dehydrochlorination of the copolymer.[28] Strong discolouration in copolymers in which CN groups predominate is observed at 85 °C in the presence of benzenesulphonic acid.[19] Zinc chloride is an effective catalyst for the polymerisation.[29]

Derivatives of acids initiate the cyclisation and discolouration. In copolymers of acrylonitrile with esters of acrylic and methacrylic acids,[30] vinyl acetate,[25–31] acrylamide,[18,32] acrylamidoxime,[18] acrolein, and methyl vinyl ketone,[33] polymerisation at the nitrile groups is more rapid and begins at lower temperatures than in the case of PAN. The cyclisation of copolymers containing methyl acrylate or methyl methacrylate units is accompanied by the elimination of methanol. The temperature at which oligomerisation at the CN group starts in an inert atmosphere is lowered when PAN contains a small quantity of acrylothiamide units. In the presence of aqueous ammonia solution, thioamide groups initiate the reaction even at 90° and lower temperatures. Conditions have been found, in which partial polymerisation at the CN groups in the macromolecules of PAN fibres containing $CSNH_2$ groups gives fibres with a high heat resistance and an appreciable modulus of elasticity at increased temperatures.[34]

Polymerisation initiators include phenols,[35] alcohols,[20,21] imides,[1] and aliphatic amines.[1,17] In the polymerisation of the CN groups of PAN, initiated by trialkylamines, at the boiling point of the solvent (dimethylformamide (DMF), dimethylacetamide DMA), polymers with comparatively little structure formation, soluble in formic acid, are obtained. The characteristic viscosity of the polymers increases when phenols are used as co-initiators.[36] The rate of cyclisation of PAN is possibly also increased by ketimine groups[17] and by the amino-groups formed in enamines by the tautomeric transformation of N-substituted imino-groups ($\rangle CH-\dot{C}=N- \rightleftharpoons \rangle C=\dot{C}-NH-$).[24]

Polymerisation at the CN groups is also initiated by alkali metal hydroxides[12,37,38] and alkoxides,[20,39] including the polymeric compounds $NaO(CH_2CH_2O)_nNa$,[38,40] aqueous sodium carbonate solution,[19] potassium cyanide,[41] and other alkaline inorganic compounds. In the presence of bases, the reaction takes place at room temperature. Initiators with basic properties also bring about other reactions of polynitriles, in particular reactions ending in chain rupture.[37]

When PAN is heated in the presence of solutions of alkali metal hydroxides in DMSO, conjugated chains of two types are formed:[42]



Under the influence of organotin compounds (tributyltin methoxide, dibutyltin dimethoxide, etc.), polymerisation at the nitrile groups of PAN and PMAN takes place at 120 °C and 70 °C respectively.[43]

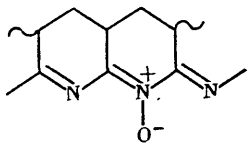
It was suggested[44] that polymerisation at the CN groups and discolouration of the polymer are initiated by β-ketonitrile groups present as defects in the PAN structure. It was later shown, however, that these groups have no significant influence on the transformations of PAN.[45]

Some authors have proposed a free-radical mechanism for the initiation of polymerisation at CN groups.[18,27,30,46]

In the absence of appreciable quantities of catalytically active impurities or structural defects, polymerisation at the CN groups may be preceded by intramolecular reactions involving the nitrile group and an α-hydrogen atom, whose products then directly initiate the polymerisation.[1,11,29] This suggestion is confirmed by the comparative stability to polymerisation of thoroughly purified PMAN, poly-α-phenylacrylonitrile, and other nitrile-containing polymers whose units do not contain mobile α-hydrogen atoms.[29]

Particular attention is being paid to the influence of atmospheric oxygen on the transformations of PAN.[9,22,47,48] It can now be taken as established that the presence of oxygen lowers the temperature threshold above which cyclisation, aromatisation, and structure formation in PAN take place.[8,22] The presence of oxygen also lowers the temperature of the start of dehydrocyanidation, intermolecular redistribution of hydrogen with the formation of

ammonia, and rupture of the polymer chains.[8,48] In addition, the reaction with oxygen leads to oxidative dehydrogenation of PAN.[8] According to Ref.44, the imino-groups in the conjugated chains are oxidised by atmospheric oxygen to give chromophoric nitrone groups, so that the colour of the polymers becomes more intense:



Carbonyl groups, which may also be formed by the hydrolysis of ketimine groups, also appear in PAN macromolecules during thermooxidative degradation.[8,12,24,44,45,49-51]

Since polymerisation at the nitrile groups is accompanied by discolouration of the polymer and a deterioration in its solubility, the use of stabilising reagents which suppress these processes may sometimes be of interest. Dienophiles (maleic anhydride, acrylamide, etc.) are effective PAN stabilisers.[52,53] The effect of these substances is based on a Diels–Alder reaction with the *cis*-azadiene sections of the polyconjugated chains;[53] this leads to rupture of the conjugated chain (a decrease in the intensity of the colour) and probably also to some extent prevents the growth of this chain. Dienophiles apparently have a stabilising action under the conditions of the thermal treatment of PAN, but do not influence the colour of the polymer which has previously been heated and kept in contact with air; they are also ineffective if the thermal treatment is combined with oxidation of the polymer, catalysed by various metal ions. This is explained by the appearance of $=\overset{+}{N}-\bar{O}$ groups in the macromolecules (see above).[53,54]

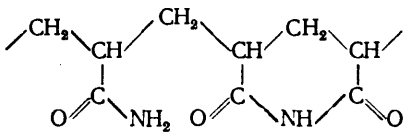
The temperature at which polymerisation of the CN groups of PAN begins is raised, and the extent to which these groups are involved in cyclisation is decreased, if small quantities of inert units (styrene, methylstyrenes, 2-vinylpyridine), dividing the polynitrile chain into relatively small blocks, are introduced into the macromolecules.[30] The inclusion of α-methylstyrene units in the macromolecules of PAN or the copolymer of acrylonitrile and vinyl acetate leads to an appreciable increase in the activation energy of the initial stage of the thermal degradation of the polymers.[55]

Intermolecular reactions involving polymerisation at the nitrile groups and trimerisation to give s-triazines can be used to harden oligomers and polymers containing infrequent (isolated) CN groups.[3]

## III. HYDRATION AND HYDROLYSIS

The hydration and hydrolysis of the nitrile groups in polymers, as in low-molecular-weight compounds,[2] takes place chiefly in the presence of acids and bases.

Treatment with 75–95% sulphuric acid converts the nitrile groups of PAN into amide, imide, and carboxyl groups.[56] The structure and properties of the reaction product depend on the original $H_2SO_4$ concentration and the other reaction conditions.[39] In the presence of 70% sulphuric acid at room temperature, polymers with a high heat resistance, consisting of acrylonitrile and acrylamide units, were obtained. The nitrile units in these polymers are present in blocks. The polymers obtained from PAN in 80–90% sulphuric acid contain 25–30% units with amide groups and 75–70% units with imide groups:



An acrylomide homopolymer could not be obtained from PAN, because in the presence of sulphuric acid the amide groups in the 1,3-positions readily undergo cyclisation. However, in the copolymer of acrylonitrile and isobutylene with the 72 : 28 composition, in which the average length of the polyacrylonitrile blocks is ~3, imidisation is suppressed to a considerable extent; in the presence of 80% sulphuric acid, the nitrile groups are almost quantitatively converted into amide groups.[39]

Treatment of PAN with 65% nitric acid at −8 °C has been used to synthesise a polymer consisting chiefly of acrylonitrile and acrylamide units,[57] with a structure similar to that of the polymer obtained from PAN and 70% sulphuric acid.[39] The nitrile groups in PAN are also hydrated by the action of concentrated hydrochloric acid in DMF [58] and on prolonged treatment in an atmosphere of hydrogen chloride.[59,60]

The use of more dilute sulphuric acid than that indicated above, in the reaction of PAN or the copolymer of acrylonitrile and isobutylene, leads to hydrolysis of the nitrile groups, that is to the formation of carboxyl groups.[39,61] Treatment of PAN with 60% $H_2SO_4$ at 95 °C gave polymers partly or completely soluble in aqueous alkali solutions. The carboxyl groups increase the rate of hydrolysis of neighbouring nitrile groups.[39] According to Ref.61, PAN with an increased isotacticity undergoes racemisation under the conditions of hydrolysis with sulphuric acid; the concentrations of iso- and syndiotactic sequences in the product were equal.

The nitrile groups in copolymers of acrylonitrile with butadiene are hydrolysed in the presence of mixtures of zinc chloride and water at 140–170 °C.[62] This reaction takes place in the vulcanisation[63] of butadiene–nitrile rubber by zinc chloride and water. The cross-linking of the macromolecules is to a large extent due to the intermolecular addition of the carboxyl groups formed in the hydrolysis to the C=C double bonds to give ester groups.

In practice, the most important polymer-analogue transformation of PAN is its alkaline hydrolysis. The water-soluble polymers obtained by hydrolysing PAN and copolymers containing more than 50% acrylonitrile groups have found extensive application as thickeners, flocculants, and protective colloids, in the preparation of coatings for textile materials, in the dressing of leather, etc.[19,64-69] The hydrolysis of PAN is most frequently carried out at 90–100 °C by NaOH and an excess of water.[70,71] The hydroxides of other alkali and alkaline earth metals, sodium silicate, trisodium and tripotassium phosphates, and sodium sulphide are also used.[72-74] The alkaline hydrolysis of copolymers of acrylonitrile with vinyl acetate in the presence of DMF, DMSO, and DMA has been described.[75] The high-temperature (180–220 °C) hydrolysis of PAN has been carried out successfully in the presence of aqueous solutions of urea, which under these conditions is hydrolysed to ammonium carbonate, which is directly responsible for the conversion of the CN groups into $CONH_2$ and $COONH_4$ groups.[76] The product of the alkaline hydrolysis of PAN is usually an aqueous solution of the polymer. To obtain

the polymer as a powder, the hydrolysis of PAN is carried out using the stoichiometric quantity of water in the presence of propan-2-ol or various other water-soluble organic substances.[77,78]

The alkaline hydrolysis of PAN takes place in two stages. In the first, heterophase, stage, the colour of the polymer changes sharply from white through dark red to yellow. In the second, homophase, stage, the intensity of the colour of the reaction mixture decreases to pale straw-yellow.[79] The change in colour is due to the characteristic mechanism of hydrolysis of the polymers, which contain blocks with nitrile-containing units arranged in sequence. Although the hydrolysis of an isolated nitrile group begins with hydration to the amide group,[2] the hydrolysis of these polymers takes place (at least to an appreciable extent) with the intermediate formation of chromophoric polyazomethine sections, which are then hydrolysed to amide and carboxyl groups. This sequence of reactions in the alkaline hydrolysis of PAN is the reason for the high initial rate of this process, which is at least ten times the rate of hydrolysis of an isolated CN group.[80]

According to this hydrolysis scheme, the change in the colour of the reaction mass in the hydrolysis of copolymers of acrylonitrile depends on the distribution of the units of the comonomers in the macromolecules.[78,80] The colour is less intense in copolymers with low values of the average length of the acrylonitrile blocks. In the case of copolymers of acrylonitrile containing methyl acrylate and vinyl acetate groups, the process begins with the hydrolysis of the ester groups. The duration of the heterophase stage in the hydrolysis of these copolymers, and also copolymers with acrylic acid, is much shorter than that observed in the hydrolysis of the homopolymer of acrylonitrile. The presence of chemically inert and hydrophobic propylene units in copolymers with acrylonitrile, on the other hand, leads to an increase in the duration of the first stage of the hydrolysis.[80] The rate of the homogenisation of the reaction mixture in the alkaline hydrolysis of PAN is also increased in the presence of surface-active substances such as methylcellulose and polyvinyl alcohol.[79] With a deficit of NaOH (less than 50–60 mole % of the concentration of nitrile units in PAN) at 95 to 100 °C, the process stops at the first stage, that is a coloured water-insoluble polymer is obtained.[79]

An important characteristic feature of the alkaline hydrolysis of cyano-containing polymers, not observed in the case of low-molecular-weight nitriles, is the existence of a limiting degree of conversion.[79–81] For example, when PAN was heated (92–96°) for a long time in the presence of an equimolar (relative to the nitrile units) quantity of alkali, that is sufficient to convert all the nitrile groups into carboxylate groups, a polymer containing sodium acrylate and acrylamide units in the molar ratio 79 : 21 was obtained. Increase in the hydrolysis time above a definite limit, in spite of the presence of free alkali, did not lead to a further increase in conversion.[79] Increase in the excess of alkali and its concentration leads only to a slight increase in the limiting conversion of nitrile groups into carboxyl groups.[79,82] The concentration of amide groups in PAN subjected to alkaline hydrolysis decreases sharply with a marked increase in the reaction temperature. Thus when an equimolar quantity of NaOH is used, the limiting conversion of acrylonitrile units into sodium acrylate units is 94% at 170°, and almost 100% at 250°.[83] The explanation for the limitation of the degree of formation of carboxylate groups is that the accumulation of $COO^-$ anions in the macromolecules during hydrolysis leads to an increase in the electrostatic repulsion between the polymer chains and the $OH^-$ anions, as a result of which the effective rate constant of the hydrolysis decreases continuously to zero.[84–86] Increase in temperature makes it possible to overcome the electrostatic repulsion, but at 140 °C an increase in the degree of degradation (rupture) of PAN molecules is observed.[82]† The inclusion of negatively charged units in the macromolecule leads to additional limitation of the degree of hydrolysis of the CN groups. For example, a study of the alkaline hydrolysis of copolymers of acrylonitrile with sodium vinyl sulphonate established that with increase in the proportion of units of the second monomer in the copolymer, there is a slight decrease in the degree of hydrolysis of the acrylonitrile units with an increase in their degree of hydration.[89] The maximum degree of conversion of nitrile groups into carboxylate groups in copolymers of acrylonitrile with methyl acrylate (17 mole %) and acrylic acid (26 mole %) was comparatively low (72–70% at 92–96 °C), in spite of the fact that in the initial period the process took place readily.[80] The low degree of conversion in these cases is evidently related to the fact that there is electrostatic repulsion between the $OH^-$ ions and $COO^-$ groups formed both from acrylonitrile units and from methyl acrylate or acrylic acid units. On the other hand, the products of the hydrolysis of copolymers of acrylonitrile containing vinyl acetate units, which are hydrolysed to uncharged vinyl alcohol units, show a slightly higher limiting degree of hydrolysis of the CN groups, compared with the hydrolysis products of PAN.[80] Under the conditions of the alkaline hydrolysis of the copolymer of acrylonitrile and vinyl acetate, in which the nitrogen-containing units show limiting conversion, the units with ester groups are converted quantitatively into vinyl alcohol groups.[78]

In the case of copolymers of butadiene and acrylonitrile (in the mass ratio 82 : 18)[90] and acrylonitrile, butadiene, and styrene (ABC-copolymer,[91] in which the nitrile groups are mostly isolated, and also cyanoethylcellulose,[92] alkaline hydrolysis is analogous to the hydrolysis of low-molecular-weight mononitriles. Nevertheless, the limiting conversion of the CN groups in the hydrolysis of the ABC-copolymer is lower than in the hydrolysis of PAN, due to steric hindrance created by the branching of the macromolecules of the graft ABC-copolymer.[91] The rate of hydrolysis of the CN group is greater than that of the de-esterification of cyanoethylcellulose.[92]

In some studies the alkaline hydrolysis of PAN is combined with secondary transformations of the polymer. Thus a process has been developed for the direct esterification of PAN[93] by the reaction of the resulting carboxyl groups with dimethyl sulphate, and also for the synthesis of a polymer containing sodium acrylate and vinylimine units, by the Hofmann reaction of the amide groups.[94] The production of a polyampholyte, whose macromolecules contain COOH and $NH_2$ groups, from PAN, aqueous NaOH solution, and bromine, is explained by the fact that initially, the reaction with alkali gives carboxylate groups and polyconjugated sections $(-\overset{|}{C}=N-)_n$, which then react with hypobromite, undergoing transformations analogous to the Hofmann rearrangement.[95]

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†The macro-chains of PAN[87] and the copolymer of styrene with acrylonitrile[88] in the presence of potassium hydroxide or t-butoxide in DMSO are broken even at room temperature. The addition of monomers polymerising by an anionic mechanism (4-vinylpyridine, propylene oxide) leads to the formation of block copolymers.

Weakly acidic cation exchangers have been obtained by treating a polyacrylonitrile fibre, consisting of acrylonitrile, methyl acrylate, and itaconic acid units (92.2:6.3:1.5), with an alkaline hydrolysing agent and hydrazine hydrate as structure-producing agent.[96]

A recent paper[97] described the hydration of the CN groups of PAN in a neutral medium in the presence of manganese(IV) oxide or Raney copper as heterogeneous catalyst. In aqueous potassium thiocyanate solutions at 80 °C, up to 50% of the nitrile groups are converted into amide groups, with a simultaneous side reaction involving polymerisation at the CN groups.

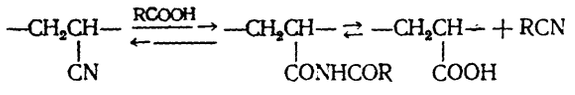
Unlike mononitriles, PAN and PMAN react with water in the absence of specially added acids or alkalis. At a temperature of 230–250 °C and a pressure of 30–40 thousand atm, these polymers react with water, becoming water-soluble;[98] it was assumed that under these conditions the nitrile groups are hydrated quantitatively to give the corresponding carbo-chain polyamides. It was later found, however, that when heated in the presence of water, PAN undergoes hydrolysis, which takes place even at 160 °C and a pressure corresponding to the vapour pressure of the components of the reaction mixture.[99] This process, like the alkaline hydrolysis, begins with polymerisation at the nitrile groups, after which the $(-\overset{|}{C}=N-)_n$ blocks are hydrolysed to give amide and carboxyl groups.[100] The ammonia liberated catalyses both these reactions and the direct hydration of the nitrile groups to amide groups according to the usual scheme characteristic of low-molecular-weight compounds. The liberation of ammonia in the hydrolysis is responsible for the autocatalytic character of the process. Because of the high temperature of the process, hydrolysis is accompanied to a slight extent by rupture of the polymer chains. The limiting degree of hydrolysis of PAN by this method is high and is 60–65% at 200 °C; the remaining groups are acrylamide groups. The existence of a limiting degree of hydrolysis in this case is related to the reversible character of the hydrolysis of the amide groups in the absence of acids or alkalis.[101]

## IV. OTHER ELECTROPHILIC REACTIONS

The CN groups in polynitriles react not only with water but also with other oxygen-containing compounds and with nitrogen- and sulphur-containing and other nucleophilic reagents.

The nitrile groups of copolymers of styrene and *p*-cyanostyrene are converted into ester groups in high yield by heating the copolymers with an excess of methanol and hydrogen chloride in tetrahydrofuran.[102] The reaction apparently involves the intermediate formation of orthoester groups. PAN undergoes direct esterification by methanol and sulphuric acid, and also of methanol, dimethyl sulphate, and catalytic quantities of sulphuric acid.[103] Like hydrolysis in the presence of sulphuric acid,[61] esterification is accompanied by racemisation.

The copolymer of styrene with acrylonitrile (in the molar ratio 61:39), in which the nitrile-containing groups are practically isolated, reacts at 160–220 °C with carboxylic acids according to the scheme



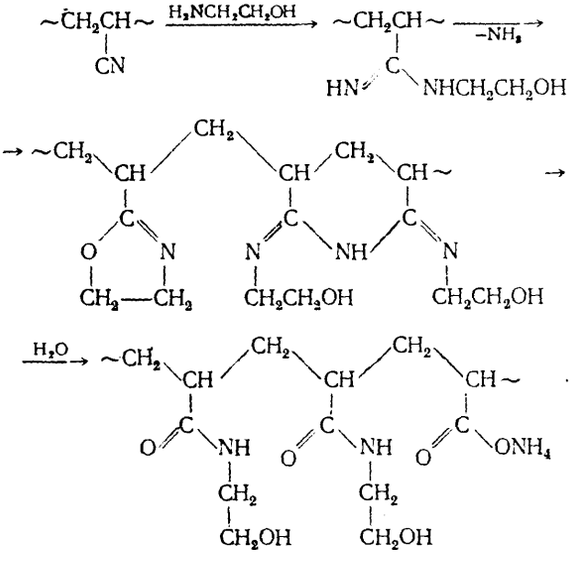
the copolymers obtained, up to 77% of the acrylonitrile units are converted into N-acylacrylamide and acrylic acid units. $T_c$ decreases on going to polymers modified by acids with higher molecular weights.[104]

Copolymers of butadiene with acrylonitrile are vulcanised by dibasic carboxylic acids in the presence of anhydrous $ZnCl_2$, which accelerates the process and also directs the reaction of the CN and COOH groups towards the preferential formation of secondary amide bridges (-CONHCO-). The frost resistance of the vulcanisates obtained is greater than that of sulphur vulcanisates.[105]

In copolymers of methacrylic acid with methacrylonitrile, the intramolecular reaction of CN and COOH groups takes place even at 150 °C to give glutarimide units.[106] When the macromolecules contain polynitrile blocks, polymerisation at the CN groups takes place simultaneously, accompanied by discolouration of the polymer.[22,106] On heating, neighbouring carboxyl-containing groups give cyclic anhydride groups. Polymers containing imide heterocycles in the macromolecules have high vitrification temperatures.[39]

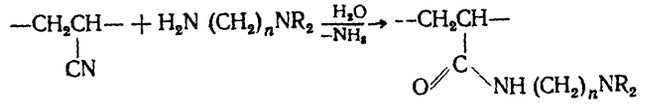
Polyacrylonitrile reacts with aniline on heating in the presence of metallic sodium or aluminium chloride to give polymers containing up to 30% N-phenylacrylamide units. The polymers isolated, which have a high proton-accepting power, also contained appreciable quantities of acrylic acid units.[107]

PAN reacts with an excess of 2-aminoethanol at 90 °C to give a water-soluble polymer.[108] The modification of PAN begins with the nucleophilic addition of 2-aminoethanol to the CN group and the formation of N-hydroxyethylamidine units. If these units are isolated, they subsequently undergo intramolecular condensation to give oxazoline fragments; neighbouring $-C(=NH)NHCH_2CH_2OH$ groups, however, as a result of condensation give N,N'-bis-(2-hydroxyethyl)glutarimidine fragments. The polymer obtained is easily hydrolysed, so that the modified units are converted chiefly into N-(2-hydroxyethyl)acrylamide and ammonium acrylate units:



Polyacrylonitrile, and also the copolymer of acrylonitrile and 5–10% vinyl acetate, in the presence of water at 115 to 120 °C reacts with an excess of N,N-dimethyl-1,3-diaminopropane or other primary–secondary primary–tertiary aliphatic diamines to give cationic polyelectrolytes, in which

dialkylaminoalkylacrylamide units predominate:[109]



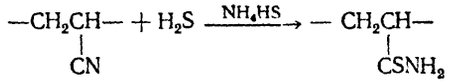
Similar transformations in these mild conditions are known for malono-, succino-, and glutaronitrile.[2] Since the mononitriles do not undergo these reactions, and polynitriles acquire a dark colour at the start of the reaction and the infrared spectrum indicates they contain C=N groups,[109] the ammonolysis–hydrolysis being considered, like alkaline hydrolysis, apparently begins with polymerisation at the C≡N groups, after which the polyconjugated sections of the macromolecules react with the amine and water.

Structured polymers have been obtained by treating PAN with hydrazine hydrate in DMF.[2,110] The cross-linking of the macro-chains is apparently partly based on the reaction of two nitrile groups with two hydrazine molecules to give 4-amino-1,2,4-triazole rings, containing macromolecular residues as substituents in positions 3 and 5.[2] Polyacrylonitrile fibres modified by treating with hydrazine are used as starting materials for further transformations,[111–114] in particular to obtain carbon fibres with good mechanical properties.[115] The modification of PAN and copolymers of acrylonitrile with aqueous solutions of hydrazine gives not only a three-dimensional network but also basic groups, which give the polymers chemisorption properties. Fibrous anion-exchangers obtained from copolymers of acrylonitrile with acrylic acid and hydrazine hydrate have a fairly high exchange capacity and are used in sorption processes.[116]

The reaction of PAN with hydroxylamine gives polyacrylamidoxime.[2,117] Polymer-analogue transformations of this polymer have been described.[118–120] Partial amidoximation of a polyacrylonitrile fibre at 90 °C has been used to obtain an anion-exchange and complex-forming fibrous sorbent.[121] The amidoximation of polyacrylonitrile chains grafted to cellulose fibres and to polypropylene has been carried out.[122]

In the reaction of PAN, copolymers of acrylonitrile and styrene or butadiene, and other CN-containing polymers, with dicyandiamide (100°, in mixtures of DMSO and methylcellosolve), more than 80% of the nitrile groups take part in the formation of 4-substituted, 2,6-diamino-s-triazine rings. The polymers obtained, containing triazine substituents in the macromolecules, have an increased thermal stability.[123]

Hydrogen sulphide adds on to the nitrile groups of PAN in DMSO or DMF in the presence of ammonium hydrogen sulphide or the salts of hydrogen sulphide with various secondary and tertiary amines as catalysts:[124]



The degree of thioamidation reaches 50–55% of the theoretical. The rate and the limiting degree of thioamidation increase with increase in the basic strength of the amine used as catalyst, and with increase in the reaction temperature. Increase in temperature, however, also increases the rate of side reactions. Thus in the reaction of PAN with hydrogen sulphide in the presence of ammonium hydrogen sulphide in DMF, more or less selective thioamidation is observed only at 0°, and at higher temperatures, amide and other functional groups are also formed.[124]

A polymer consisting of acrylonitrile and acrylothioamide units was also obtained by treating PAN with ammonium hydrogen sulphide alone in DMF. The polymer modified in this way retains its linear structure.[125] A modified polymer containing 7 mole % thioamide groups was used to obtain fibres.[126] Thioamide groups have been introduced into a prepared PAN fibre by treating it with aqueous solutions of ammonium[127] or sodium[128] sulphides, leading to a marked increase in the heat resistance and the stability of the fibre to repeated deformation at high temperatures. According to Ref.129, nitrile-containing fibres thioamidated with sodium sulphide solution have a high sorptive power with respect to the platinum group metals.

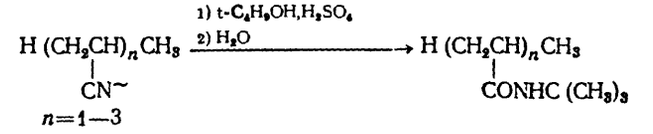
The addition of hydrogen sulphide to the nitrile groups of poly-α-chloroacrylonitrile has been described.[130] As in the polymerisation of the CN groups of PAN and in its alkaline hydrolysis, acrylic acid, methyl acrylate, and vinyl acetate units have an activating action on the thioamidation, whereas the rate of the thioamidation is decreased when the macromolecules contain styrene units.[131] Moreover, the initial effective rate constant for the thioamidation of the CN groups of PAN is 10–100 times that for the thioamidation of acetonitrile. This constant decreases rapidly, however, with increase in the degree of transformation of the CN groups.[132] Thus there is an analogy between thioamidation and various other reactions of polynitriles examined above. On this basis, and in view of the ability of thioamide groups to initiate polymerisation at the CN groups, it may be assumed that the thioamidation of polynitriles, like their alkaline hyrolysis, takes place at least partly via a stage involving the intra- and intermolecular cyclisation of CN-containing polymers.

The electrophilic reactions of nitrile groups in polymers also include reactions leading to the formation of a new C–C bond, for example the reaction of butadiene–nitrile rubber with resorcinol in the presence of HCl and $ZnCl_2$ (Hoesch synthesis), as a result of which up to 10% of the acrylonitrile units are converted into vinyl 2,4-dihydroxyphenyl ketimine units, and as a result of subsequent hydrolysis into vinyl 2,4-dihyroxyphenyl ketone units.[133] Polymers containing ketimine and ketone groups have also been obtained by the reactions of Grignard reagents with the copolymer of styrene and *p*-cyanostyrene,[102] and also PAN.[45]

## V. NUCLEOPHILIC AND OTHER REACTIONS

In recent years it has been possible to carry out the polymer-analogue transformations of polynitriles using the most familiar nucleophilic reaction of CN groups, namely the Ritter reaction.

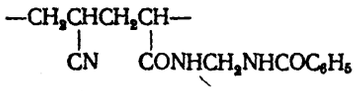
In the reaction of compounds which are low-molecular-weight models of PAN with t-butyl alcohol in tetramethylene sulphone in the presence of sulphuric acid at 25–40 °C, the nitrile groups are converted in high yield into N-t-butyl amide groups:



On going from the monomeric to the dimeric and trimeric models, the rate constant increases to a very slight extent that is in this reaction the neighbouring groups have no significant influence on the reactivity of the CN groups.[13] A study of the reaction of high-molecular-weight PAN with t-butyl alcohol under the same conditions established that the reaction has a limiting degree of transformation (abou 55%), which increases with increase in temperature and v decrease in the concentration or molecular weight of the original PAN. The polymer obtained has a much highe

than the original PAN, and the heat resistance of the modified polymer is determined by the degree of transformation of the nitrile groups.[135]

In tetramethylene sulphone in the presence of sulphuric acid, the CN groups of PAN undergo the Ritter reaction with N-hydroxymethylbenzamide, N-hydroxymethylphthalamide, and other N-hydroxymethyl-substituted amides and imides.[136] The polymers formed, for example

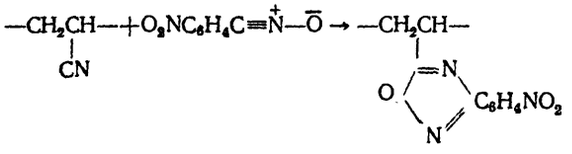


unlike the corresponding homopolymers obtained by radical polymerisation, for example poly(N-benzamidomethylacrylamide), show a greater tendency to undergo structure formation, and this is attributed, in particular, to the liberation of formaldehyde under the conditions of the polymer-analogue transformations and its reactions with the CN groups of different macromolecules to give methylene-bis-amide bridges



The vulcanisation of copolymers of butadiene, acrylonitrile, and vinylidene chloride at 142 °C under the influence of anhydrous zinc oxide is possibly based on the nucleophilic reactivity of the nitrile group.[137] The presence of ZnO leads to the partial dehydrochlorination of the vinylidene chloride units, and the $ZnCl_2$ (or $HZnCl_3$) catalyses the subsequent formation of the N–C bond as a result of the reaction of the nitrogen of the CN group with the carbon atom of another polymer chain having an increased electrophilic reactivity.

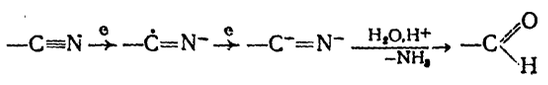
The 1,3-dipolar cyclo-addition of 4-nitrobenzonitrile oxide to the CN groups of copolymers of acrylonitrile with styrene and with vinylidene chloride, giving 1,2,4-oxadiazole heterocycles, was recently described:[138]



The syntheses were carried out in γ-butyrolactone by heating at 130 °C the copolymer with the chloride of 4-nitrobenzohydroxamic acid, which under these conditions undergoes dehydrochlorination to the nitrile oxide. The degree of conversion of the nitrile groups is 30–50%.

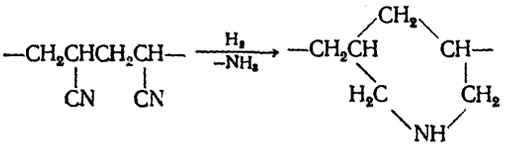
The reduction of the CN groups of polymers to aldimine or amino-groups has been described. The nitrile groups of carbo-chain polymers are partly reduced by tin(II) chloride in the presence of hydrogen chloride to aldimine groups, which on subsequent hydrolysis are converted into aldehyde groups (the Stephen reaction).[2] The use of this reaction to modify butadiene–nitrile rubber leads to an increase in the strength of the vulcanisates.[139]

The reduction of the nitrile groups in macromolecules by the radical-ions formed in the reaction of metallic sodium with naphthalene or hexamethylphosphoramide has been described. Aldehyde groups are produced in the polymers:[140]



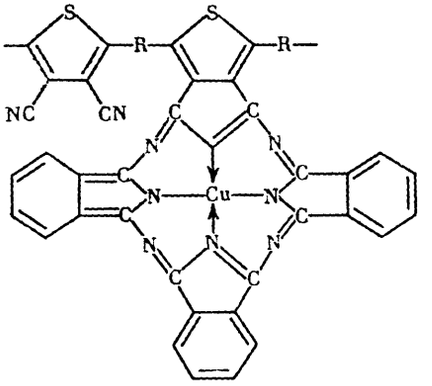
The intermediate products of this reaction initiate the graft polymerisation of styrene and methyl methacrylate, evidently an anionic mechanism.

In the presence of Raney nickel or other catalysts, the CN groups of PAN dissolved in DMF are partly hydrolysed (140–185 °C, 65–185 atm).[56,141] Since the CN groups occupy the 1,3-positions in the macromolecules, hydrogenation is accompanied by cyclisation, to give mainly piperidine rings:



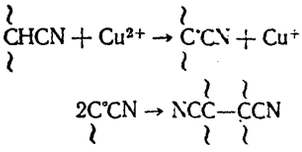
Acrylamide and acrolein units were also found in the modified polymer.

When hetero-chain polyamides whose chains contain 3,4-dicyanothiophene rings are heated (200–250 °C) with 1,2-dicyanobenzene and copper acetylacetonate, approximately 50% of the dicyanothiophene units are converted into phthalocyanine-like units:



The polymers obtained have an increased thermal stability.[142]

Butadiene–nitrile rubbers are cross-linked in the presence of copper(II) salts by a free-radical mechanism. The >CHCN group probably forms with $Cu^{2+}$ a redox system in which there is one-electron transfer from the polarised CH bond to the cation, and the recombination of the radicals obtained leads to structure formation in the polymer:[143]



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The the reactions of nitrile-containing polymers can be divided into three groups. The first group consists of reactions taking place according to schemes familiar for low-molecular-weight nitriles. Because of the difference in the steric, polar, and other factors, the quantitative characteristics may differ considerably for the reactions of the low- and high-molecular-weight compounds. The second group also consists of reactions familiar for low-molecular-weight compounds, but in this case the transformations of the high- and low-molecular-weight compounds take place by different schemes. The third group consists of reactions which are specific for nitrile-containing polymers. The reactions of practical importance involving cyclisation and

polymerisation (third group) and various hydrolysis reactions (second group), for which reliable schemes for the transformations of the CN groups have been established, are now being studied in most detail, and methods for the control of these transformations have been developed. There is comparatively little published information, however, on the electrophilic reactions of polynitriles with various oxygen-containing (except water), nitrogen-containing, and other reagents, or on the nucleophilic reactions of polynitriles. In view of the reactivity of the CN group and the extensive use of compounds containing this group in synthetic organic chemistry, the possible applications of polynitriles as starting materials for the production of new polymers are far from exhausted. Since polynitriles are readily available, the detailed study of the known reactions of these polymers and the further extension of the range of reagents used for modification will undoubtedly produce promising results.

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# Electronically Excited Atoms and Molecules in Solid-Gas Systems

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The formation, emission, and deactivation of electronically excited atoms and molecules in solid-gas systems have been examined. The mechanisms of these processes and the influence of the nature of the solid on their course have been discussed. The bibliography contains 175 references.

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## I. INTRODUCTION

In recent years there has been a marked increase in interest in the study of excited states on a surface and in particular electronically excited atoms and molecules in heterogeneous systems. This is related to the development of plasma and radiation chemistry, laser technology, and photocatalytic processes, in which the participation of electronically excited atoms and molecules is obvious, although it has been insufficiently studied.[1] Moreover, there are experimental data which indicate that electronically excited molecules are formed in thermal heterogeneous processes. In particular, certain reactions take place by a heterogeneous–homogeneous mechanism, that is electronically excited atoms and molecules are emitted into the gas phase in the course of the reaction. Thus it is clear that for an understanding of the mechanism of many heterogeneous reactions in a solid–gas system it is important to know the properties and behaviour of electronically excited atoms and molecules.

The present review deals primarily with long-lived species. The long radiative lifetimes of some electronically excited atoms and molecules in the gas phase suggest that on solid surfaces also, their stability will be sufficient for them to take part in surface processes such as the luminescence of adsorbed molecules and the formation and emission of electronically excited atoms and molecules from solid surfaces under the influence of light, chemical, mechanical, and other factors. The results of the study of the deactivation of electronically excited atoms and molecules on solid surfaces of different kinds are of considerable interest. The deactivation is due to the exchange of the excitation energy with the solid or with an adsorbed layer, and also to chemical reaction with the surface of the adsorbent (chemisorption) and with the adsorbed species—molecules and radicals.

Information of different kinds on the behaviour of various electronically excited atoms and molecules at a solid–gas interface has been published. The experimental data are generally qualitative in character. The largest number of publications in this field has been devoted to electronically excited oxygen molecules (singlet oxygen $^1O_2$); data have also been published on electronically excited nitrogen molecules, metal atoms, and metastable inert gas atoms.

## II. THE FORMATION AND EMISSION OF ELECTRONICALLY EXCITED ATOMS AND MOLECULES INTO THE GAS PHASE FROM A SOLID SURFACE

Recent reviews[1-11] contain varied information on the formation of electronically excited atoms and molecules and their emission from solid surfaces. New data, not discussed in these reviews, have recently been published[12,13] on the mechanism of the photosensitised formation of singlet oxygen in solid–sensitiser–oxygen systems. It has also been found[15-18] that emission of singlet oxygen from solid surfaces takes place in many dark and photo-heterogeneous processes. The surface and the adsorption layers have been excited by different methods: the chemical reaction of oxygen atoms with metal oxides,[17,19-21] mechanochemical processes,[15] the thermal decomposition of catalysts,[16,23] the illumination of catalysts containing transition metal ions,[18,24,25] etc.

### 1. The Photosensitised Formation of Electronically Excited Oxygen Molecules in Heterogeneous Systems

The idea that singlet oxygen ($^1O_2$) is formed in the reaction of a triplet dye molecule with oxygen by the transfer of the triplet excitation energy was first put forward by Kautsky,[26] who observed the simultaneous quenching by oxygen of the phosphorescence of trypaflavine adsorbed on silica gel and oxidation of the leuco-base of Malachite Green, adsorbed on other silica gel granules. The oxidation took place in a narrow pressure range $(1.56-3.12) \times 10^{-3}$ hPa† oxygen. It was suggested that the oxidation involved electronically excited oxygen molecules, formed by the reaction

$$T + {}^3O_2 \rightarrow S_0 + {}^1O_2$$

where T and $S_0$ represent respectively the triplet-excited and ground states of the dye molecule, and $^3O_2$ and $^1O_2$ the ground and singlet-excited states of oxygen. Since the sensitiser and the substrate being oxidised were separated in space, the singlet oxygen could pass into the gas phase. It should be noted, however, that the oxidation stopped when the distance between the particles with the adsorbed dye sensitiser and with the substrate being oxidised was increased to several millimetres.

The discussion of the nature of the oxidising agent in these systems continued for many years. Thus according to the hypothesis of Weiss,[27] the oxidising agent could be the oxygen radical-anion $O_2^{\cdot-}$. Later, Weiss adopted the views of Franck and Livingston,[28] who suggested that hydrogen peroxide is formed in this process. The radical-anion removes a hydrogen atom either from the dye sensitiser[28] or from a water molecule adsorbed on silica gel.[29] As pointed out by Terenin,[30] however, energy considerations indicate that the $O_2^{\cdot-}$ radical-anion cannot oxidise the leuco-compound, and the formation of hydrogen peroxide should lead to an irreversible chemical change in the dye sensitiser. The energy of the triplet level of trypaflavine (48 kcal mole$^{-1}$) is insufficient for the removal of a proton from water molecules adsorbed on silica gel.[31] In the opinion of other authors,[32,33] the reactive species is a metastable complex (moloxide) formed by the triplet dye molecule with oxygen. Under the conditions of Kautsky's experiment, however, this complex cannot leave the surface and reach the substrate being oxidised.

Rosenberg and co-workers[34,35] studied the influence of gases on the quenching by oxygen of the phosphorescence of trypaflavine adsorbed on silica gel, and suggested that a vibrationally excited oxygen molecule is formed in the reaction of oxygen with the triplet sensitiser molecule.

Recently, a number of workers have interpreted the data obtained in the study of systems of this kind in terms of singlet oxygen formation.

Thus the dye-photosensitised (including trypaflavine-sensitised) decrease in the strength of textile fibres has been attributed[29,36] to the participation of singlet oxygen. This effect was observed in the absence of water at an oxygen pressure of $10^{-3}$ hPa; the sensitiser (a film of dye or a coloured fibre) was situated at a distance of several millimetres from the textile fibre being oxidised.

The dye- (eosin and Methylene Blue) sensitised oxidation by oxygen of diphenylanthracene and rubrene, separated from the sensitiser by layers of barium or cadmium stearate with different thicknesses (up to 500 Å), has been studied.[37] In the opinion of the authors cited, singlet oxygen is formed in this case, and can diffuse through the stearate layers and oxidise the substrate molecules.

The oxidation of various organic substances in solution, photosensitised by dyes (Rose Bengal, eosin, fluorescein, etc.) deposited on chloromethylated polystyrene, has been studied.[38] Analysis of the products indicated that the oxidation is brought about by singlet oxygen, formed in the reaction of a triplet dye molecule with oxygen.

The oxidation of anthracene and 2-methylbut-2-ene in solution, photosensitised by Rose Bengal and eosin deposited on Amberlite IRA-400 ion exchange resin and by Methylene Blue deposited on Amberlite IRS-200, has been observed.[39] From the fact that the compounds obtained were identical to the products of oxidation by singlet oxygen, it was concluded that singlet oxygen is involved in the reaction.

The oxidation of tetramethylethylene, 1,3-diphenylisobenzofuran, etc. in solution, photosensitised by Rose Bengal and Methylene Blue adsorbed on silica gel and alumina gel, has been studied.[40] The efficiency of the oxidation was approximately the same in heterogeneous and homogeneous systems. The experiments of Ref.26 were also repeated using Rose Bengal adsorbed on silica gel as the sensitiser, and 9,10-diphenylanthracene adsorbed on other silica gel particles as the substrate being oxidised. When oxygen (pressure 6 hPa) was passed through a "fluidised bed" of the catalyst with illumination by a xenon lamp for 2.5 h, the degree of oxidation was 50%. It was suggested that the oxidation involves singlet oxygen.

The photosensitised formation of singlet oxygen has been detected[41,42] using a thin film of Rose Bengal as sensitiser. The conclusion that singlet oxygen is formed was reached by analysing the oxidation products of rubrene.

The photo-oxidation of the surface of a single crystal of anthracene in an oxygen atmosphere has been studied.[43] The composition of the products indicated that the reaction takes place under the influence of singlet oxygen.

Thus the conclusion that singlet oxygen plays a decisive role in photosensitised oxidation in heterogeneous solid–dye–oxygen systems was based on the fact that the products of the photosensitised oxidation and the direct action of singlet oxygen were identical. The corresponding comparison for solutions was first made in Refs.44 and 45. Other workers[46,47] studied the oxidation of substances deposited on various supports (cellulose, silica gel, etc.) by singlet oxygen, obtained in different ways. Thus in Ref.46, various substances adsorbed on silica gel were oxidised by singlet oxygen formed by heating the triphenyl phosphite–ozone adduct. The products obtained by oxidising tryptophan, thymine, and uracil, adsorbed on silica gel, by singlet oxygen obtained in a radiofrequency discharge were also identified. In Ref.47, 9,10-dimethylanthracene and other substances,

† 1 hPa = 100 Pa ≅ 0.75 Torr (Editor of Translation).

adsorbed on cellulose and silica gel, were oxidised using singlet oxygen formed in a ultrahigh-frequency discharge. On the basis of these studies, it was suggested[48] that photosensitised oxidation in systems with the sensitiser and the substrate being oxidised separated in space could be used to test for the formation of singlet oxygen. It is only recently, however, that is has been possible to observe the luminescence of singlet oxygen ($^1\Delta_g$) in the gas phase with photosensitisation by a dye film (Rose Bengal).[49,50]

Recently, semiconducting detectors were used to detect singlet oxygen in the gas phase.[17,51] This method is based on the change in the electrical conductivity of thin oxide films (ZnO, $TiO_2$, CdO, etc.) as a result of the adsorption of atoms and molecules.[22,114,134] The procedure requires the use of not only semiconducting films but also additional apparatus and methods for the selective determination of the concentration of the gas being determined. Singlet oxygen is detected in the presence of oxygen atoms using an apparatus in which the oxygen atoms are deactivated on the surface of mercury or silver oxides.[17,51] The influence of ordinary (triplet) oxygen can be practically eliminated either by lowering the temperature of the detector or by oxidising it beforehand.[51,113] In Ref.12, semiconducting detectors, and also calorimetry, showed unambiguously that the illumination of dyes (trypaflavine, Rose Bengal) adsorbed on quartz, and a film of trypaflavine, leads to the formation and emission of singlet oxygen into the gas phase.

The proof that singlet oxygen is formed when heterogeneous solid–sensitiser–oxygen systems are illuminated, and the quenching of the phosphorescence of the adsorbed sensitiser, observed simultaneously, confirm the view[26] that singlet oxygen is formed by the reaction of oxygen with a triplet molecule of the sensitiser. It should be noted, however, that the quenching of the phosphorescence of the sensitiser by oxygen indicates only that singlet oxygen is formed, and to investigate its subsequent behaviour (the regular features of emission into the gas phase) it is necessary to study its desorption.

Since the concentration of singlet oxygen in the gas phase is directly proportional to the intensity of excitation,[12] the change in the intensity of the phosphorescence of the adsorbed sensitiser in the reaction with oxygen is apparently given by an equation of first order with respect to the triplet molecules of the sensitiser.[34,52] The change in the intensity of the phosphorescence of the adsorbed sensitiser with change in the oxygen pressure[35] corresponds to the change in the concentration of singlet oxygen in the gas phase. Thus the intensity of the phosphorescence of the sensitiser decreases, and the concentration of singlet oxygen in the gas phase increases, with increase in the oxygen pressure. With further increase in the oxygen pressure, the intensity of the phosphorescence of the sensitiser becomes close to zero (that is all the triplet molecules of the sensitiser are quenched), but the concentration of singlet oxygen formed is a maximum, and its concentration in the gas phase is determined only by homogeneous–heterogeneous deactivation processes.[12,13] The rate constant for the reaction of a triplet molecule of trypaflavine adsorbed on quartz is $5 \times 10^9$ litre $mole^{-1}s^{-1}$. The calculation was based on the assumption that the singlet oxygen is formed by the transfer of the energy of the sensitiser molecule to oxygen in a short-lived collision complex. This value agrees satisfactorily with published data[34,52,53] obtained by measuring the quenching by oxygen of the phosphorescence of trypaflavine adsorbed on silica gel. In the works cited it was again assumed that the quenching of the phosphorescence of the sensitiser by oxygen takes place in a short-lived collision complex formed by the triplet molecule of the sensitiser and oxygen.

In this case also, however, it is necessary to take account of the specific features of heterogeneous systems. Thus the quenching of the phosphorescence of trypaflavine adsorbed on silica gel does not obey the Stern–Volmer relationship. In Refs.53–59, the regular features of the change in the intensity of the phosphorescence and the lifetime of the triplets of trypaflavine adsorbed on silica gel with change in the oxygen pressure in the gas phase were explained in terms of the dynamic character of the quenching (according to Terenin[60]), that is the process takes place in a short-lived collision complex. Thus from the practically instantaneous and ready reversal of the quenching as far as −60 °C it was concluded[55] that the form of the quenching curves is independent of the adsorption of oxygen. In Ref.53 it was established that all the luminescence centres of trypaflavine adsorbed on silochrome react with oxygen at the same rate at all stages of the non-exponential quenching of the phosphorescence, and it was concluded that the quenching is dynamic in character. In Refs.54 and 56–58 the deviations from the Stern–Volmer relationship were attributed to the molecular-sieve and trajectory effect. The sensitiser molecules may be situated in macro-pores of the adsorbent, readily accessible to oxygen, or in micro-pores (cracks), which are not readily accessible. The distribution of the sensitiser in the macro- and micro-pores determines what fraction of the triplet molecules of the sensitiser will contribute to the phosphorescence, and what fraction will be quenched. It is difficult to imagine, however, that a pore which is accessible to the fairly large molecule of the sensitiser (trypaflavine) will not be filled by oxygen molecules, whose dimensions are appreciably smaller. Moreover, it was assumed that only part of the trajectory of the random movement of the active product of the photodissociation of the trypaflavine molecule (polaron, H, exciton, etc.) in the matrix is accessible to oxygen molecules. Thus in the opinion of the authors cited, the nature of the solid on which the sensitiser is adsorbed has a decisive influence on the quenching of the phosphorescence of the sensitiser (and hence the formation of singlet oxygen). As noted in Ref.53, the regular features of the quenching of the phosphorescence of adsorbed trypaflavine can also be explained by assuming that there is a distribution of the luminescence centres with respect to lifetime. This view was put forward in Ref.61. It was found that trypaflavine is adsorbed as monomers and dimers, and that the lifetime of the triplets in the dimeric form is shorter than for the monomeric form. Moreover, the lifetime of the triplets of the adsorbed trypaflavine was independent of the oxygen pressure over a wide range ($10^{-6}$–1 hPa), whereas the intensity of the phosphorescence changed by several powers of ten. It was therefore suggested that a decisive role in the quenching of the phosphorescence of adsorbed trypaflavine is played by adsorbed oxygen. In Ref.62, the quenching of the phosphorescence of biphenyl, naphthalene, and chloronaphthalene on silica gel was brought about by adsorbed oxygen, that is the quenching was static in character.

There are thus two views of the quenching of the phosphorescence of adsorbed molecules by oxygen and the associated formation of singlet oxygen. Up to the present (see earlier reviews[2–11]) the predominant view has been that singlet oxygen is formed in a short-lived collision complex (triplet sensitiser molecule–oxygen), that is the dynamic mechanism of the quenching of the phosphorescence has been assumed. Recently, however, direct proof that adsorbed $O_2$ molecules take part in the formation of singlet oxygen has been obtained. Thus in Refs.12 and 13 it was shown that singlet oxygen is formed with the photosensitisation of trypaflavine adsorbed on quartz, or a film of trypaflavine, and previously adsorbed oxygen.

The formation and emission of singlet oxygen into the gas phase was observed under conditions of continuous evacuation at a residual gas pressure of $10^{-6}$ hPa, and the intensity of the emission decreased regularly with time. The emitting power of these systems was preserved for several tens of minutes, evidently due to oxygen adsorbed on the surface. At an oxygen pressure in the gas phase of $10^{-6}$ hPa, the quenching of the phosphorescence of adsorbed trypaflavine is not observed.[35] Moreover, singlet oxygen is not formed if the sensitiser is evacuated for several hours at a temperature of ~100 °C.

Similar data were obtained using vanadium[24] and molybdenum[25] ions deposited on quartz as sensitiser. The results of these experiments show convincingly that adsorbed oxygen plays a decisive role in the formation of singlet oxygen in heterogeneous systems. The residence time of the oxygen molecule on the solid surface, even in the case of physical adsorption, is greater by several powers of ten than the lifetime of the collision complex, so that the efficiency of the formation of singlet oxygen should be greater by several powers of ten in this case. Thus in the gas phase the efficiency of the formation of singlet oxygen is ~$10^{-3}$ (from data on the quenching of the phosphorescence of the sensitiser[9]), whereas in solutions it is close to 1, because of the cage effect.[63-65] In Ref.40 it was shown that the efficiency of the photosensitised oxidation in heterogeneous systems is not lower than that under homogeneous conditions for solutions. According to Ref.61, for trypaflavine adsorbed on silica gel, the efficiency of the formation of singlet oxygen is close to 1. The question of possible centres for the adsorption of oxygen can be considered. It may be assumed that oxygen is adsorbed on the surface of the solid, migrates over the surface, and collides with triplet molecules of the sensitiser. Simple calculation of the concentration of singlet oxygen in the gas phase shows, however, that in this case the efficiency of its formation should be much smaller than 1. It is natural to assume that the oxygen molecules involved in the quenching are adsorbed on the molecules of the sensitiser.

The quenching by oxygen of the phosphorescence of trypaflavine adsorbed on silica gel is a practically activationless process.[34,53] On the other hand, in Refs.12 and 13 it was found that the concentration of singlet oxygen in the gas phase increases considerably with increase in the temperature of the sensitiser. The concentration of singlet oxygen in the gas phase is apparently determined by the desorption of singlet oxygen from the surface. It is still not clear from which centres the singlet oxygen is desorbed, that is whether it is desorbed from a sensitiser molecule or from the quartz surface. The increase in the concentration of singlet oxygen in the gas phase with increase in the temperature of the sensitiser, detected in Ref.13, can be attributed to a decrease in the residence time of the singlet oxygen molecule either on the quartz surface or on the sensitiser molecule. Correspondingly, the activation energy of the effective rate constant for the formation of singlet oxygen, 10 kcal mole$^{-1}$,[13] can be taken as the heat of adsorption of singlet oxygen on the quartz surface or as the heat of adsorption on the sensitiser molecule. In Ref.34, the quenching by oxygen of the phosphorescence of trypaflavine adsorbed on silica gel stopped at the temperature of liquid nitrogen. The heat of adsorption of singlet oxygen, calculated with allowance for this experimental fact, was found to be 6 kcal mole$^{-1}$. Unfortunately, there are no direct data on the adsorption characteristics of singlet oxygen.

Thus it is not yet possible to give a definite answer to the question raised. The estimated activation energy of the desorption of oxygen from the surface of trypaflavine (12 kcal mole$^{-1}$),[66] however, indicates that desorption of singlet oxygen from the sensitiser molecule is more probable.

A possible scheme for the formation and emission of singlet oxygen into the gas phase is given below:

$$^1S_0 + {}^3O_2(gas) \rightleftarrows [^1S_0 \ldots {}^3O_2(ads)]$$
$$[^1S_0 \ldots {}^3O_2(ads)] \xrightarrow{h\nu} [^1S_1 \ldots {}^3O_2(ads)]$$
$$[^1S_1 \ldots {}^3O_2(ads)] \rightarrow [^3S_1 \ldots {}^3O_2(ads)]$$
$$[^3S_1 \ldots {}^3O_2(ads)] \rightarrow [^1S_0 \ldots {}^1O_2(ads)]$$
$$[^1S_0 \ldots {}^1O_2(ads)] \rightarrow {}^1S_0 + {}^1O_2(gas)$$

where $[^1S_0 \ldots {}^3O_2(ads)]$, $[^1S_1 \ldots {}^3O_2(ads)]$, $[^3S_1 \ldots {}^3O_2(ads)]$, and $[^1S_0 \ldots {}^1O_2(ads)]$ are the complexes of oxygen with the sensitiser molecule in the ground state $^1S_0$, the singlet excited state $^1S_1$, and the triplet state $^3S_1$, and $^3O_2(gas)$, $^1O_2(gas)$, $^3O_2(ads)$, and $^1O_2(ads)$ the ground and singlet excited states of oxygen in the gas phase and in the adsorbed phase respectively. The nature of the complex in which singlet oxygen is formed must be determined in each specific case.

Until recently it was usually assumed that singlet oxygen is formed in a short-lived collision complex with transfer of energy,[9] and not in a complex with charge transfer, except in the case of aromatic substances.[67] It has been found, however, that the formation of singlet oxygen in a complex with charge transfer is characteristic of alkenes[10] and a number of other substances.[4,68] As noted in Ref.69, the detection of magnetic effects (the influence of a magnetic field and chemical polarisation of the nuclei) in a number of cases helps to decide between energy transfer and electron transfer processes. A detailed review of the influence of a magnetic field on the reaction of triplet molecules with oxygen has been published.[70] There is apparently only one published paper on the influence of a magnetic field on the efficiency of the formation of singlet oxygen in heterogeneous systems. This is a paper by Frankevich and Sokolik[71] on the solid-phase photo-oxidation of tetracene. The reaction of oxygen with tetracene molecules in the triplet state gives a charge-transfer complex with a lifetime of 10 s at room temperature. The application of a magnetic field ($H$ = 2 kOe) increases the rate constant for the reaction of oxygen with the triplet molecule of tetracene (that is the efficiency of the formation of singlet oxygen) by 50 ± 10%. The authors cited consider that all the singlet oxygen formed is used up in the oxidation of tetracene. The existence of emission by singlet oxygen from the surface of tetracene into the gas phase does not cast doubt on the main conclusions of the work cited, but it must be taken into account in the explanation of the temperature dependence of the rate of the photo-oxidation of tetracene.

This work clearly demonstrates the important information that can be obtained by studying the influence of a magnetic field on the efficiency of the formation of singlet oxygen in heterogeneous systems.

In Ref.4 it was suggested that singlet oxygen is formed via an intermediate moloxide stage. In a recent theoretical paper,[72] the quenching of the phosphorescence of ethylene by oxygen (and the formation of singlet oxygen) was also attributed to moloxide formation.

It is also possible to use inorganic molecules deposited on a solid surface as sensitiser. Thus when a quartz surface promoted by vanadium[18,24] or molybdenum[25] ions is illuminated in the presence of oxygen, singlet oxygen is formed and emitted into the gas phase. From the regular features of the emission of singlet oxygen in $V/SiO_2$ and $Mo/SiO_2$ systems, and also from data on the quenching by oxygen of the phosphorescence of transition metal (vanadium, molybdenum) ion complexes on a quartz surface,[73] the following mechanism can be proposed for the formation and emission of singlet oxygen into the gas phase in these systems.[18,24] When the $V/SiO_2$

system is illuminated, surface charge-transfer complexes are formed:[74]

$$|V^{5+}O^{2-}| \xrightarrow{h\nu} |V^{4+}O^{-}|_s^*$$

where s = surface. In the quenching of the phosphorescence of the complex on the surface of the adsorbent, the excitation energy of the complex is transferred to the adsorbed oxygen molecule to give singlet oxygen, which is subsequently desorbed. In this case the dependence of the concentration of singlet oxygen in the gas phase on the intensity of the exciting light and the oxygen pressure is similar to that for solid–dye–oxygen systems.[12,13] A decrease in the concentration of the metal–oxygen complexes on the quartz surface, brought about by preliminary photo-reduction of the specimen with hydrogen (when the V and Mo complexes decompose[75]), leads to a decrease in the intensity of the liberation of singlet oxygen.

With increase in the temperature of the sensitiser, the concentration of singlet oxygen in the gas phase increases. The activation energy of this process is 1.5 kcal mole$^{-1}$. This value is appreciably lower than the activation energy of the formation and emission of singlet oxygen into the gas phase when a dye (trypaflavine) is used as sensitiser.[13] It has been suggested[24] that the increase in the intensity of the emission of singlet oxygen with increase in the temperature of the sensitiser in this case is related to a decrease in the residence time of the singlet oxygen on the surface of the adsorbent, and to a consequent decrease in the rate of the deactivation of singlet oxygen on the solid surface.

Thus in the investigation of the mechanism of photo-oxidative processes on deposited catalysts it is apparently necessary to take account of the extremely probable role of singlet oxygen molecules. It also follows from Refs.15, 18, 24, and 25 that some oxidative photo-heterogeneous processes may take place by a heterogeneous–homogeneous mechanism.

## 2. The Influence of the Nature of the Sensitiser Carrier on the Efficiency of Formation of $^1O_2$

There are practically no published data on the influence of the solid on the photosensitised formation and emission of singlet oxygen into the gas phase. In a number of cases it is difficult to relate unambiguously the change in the efficiency of the formation of singlet oxygen to a specific mechanism of the influence of the solid.

Thus for example the quenching of the phosphorescence of trypaflavine adsorbed on silica gel does not obey an exponential law.[77–79] In Ref.77, the phosphorescence quenching curves were represented as the sum of two exponents, corresponding to two metastable levels of the sensitiser molecule. In Ref.79 this suggestion was rejected on the basis of the fact that the phosphorescence quenching curve is non-exponential at low temperatures, when the lifetime and phosphorescence spectra are independent of temperature. The non-exponential nature of the quenching of the phosphorescence, which could not be represented as the sum of two exponents, was attributed to a difference in the nature of the trypaflavine adsorption centres on the silica gel.

In Ref.82 it was found that the kinetics of the quenching of the phosphorescence of naphthalene and anthracene adsorbed on $\gamma$-$Al_2O_3$ at degrees of covering $\ll 1$ do not obey an exponential law, but are described by a sum of two exponents. The observed regular features were attributed to a difference in the nature of the adsorption centres. In Ref.78, a mechanism for the quenching of the phosphorescence was proposed, involving the reversible dissociation of the excited sensitiser molecule and the migration of one of the products ($HO_2$, $H^+$, exciton, etc.) in the cage. In Ref.61, the deviation from the exponential relationship was attributed to the presence of monomeric and dimeric forms of the sensitiser. The phosphorescence which was quenched rapidly was assigned to sensitiser dimers, and that which was quenched more slowly was assigned to the monomers. This view is confirmed by the fact that the changes in the absorption and luminescence spectra of trypaflavine adsorbed on silica gel are slight compared with aqueous solutions, indicating that trypaflavine is physically adsorbed on the silica gel surface.[77] This is also indicated by the fact that the form of the phosphorescence quenching curve is independent of the pH at which the adsorption is carried out.[79] In Refs.80 and 81 it was shown that the chemisorption of the dye takes place only if the overlap integral of the wavefunctions of the adsorbate and the adsorbent is sufficiently large to displace the hydrogen bond.

In Ref.61, therefore, the form of the curve for the quenching by oxygen of the phosphorescence of adsorbed trypaflavine was attributed to a difference between the efficiencies of the reaction of oxygen with the triplets of trypaflavine in the monomeric and dimeric forms (and hence a difference in the efficiences of the formation of singlet oxygen). The values are 0.980 ± 0.05 for the monomeric form, and 0.86 ± 0.04 for the dimer.

A decrease in the sensitivity of the phosphorescence of adsorbed trypaflavine to the presence of oxygen on dehydroxylation of the silica gel has been observed.[55] The opposite conclusion was reached, however, in a study[83] of the influence of the moisture content and nature of the support on the quenching by oxygen of the phosphorescence of various adsorbed organic substances (including substances adsorbed on silica gel).

It was also found[18,25] that adsorbed vanadium and molybdenum ions are good sensitisers of the formation of singlet oxygen, but when an oxide phase appears, singlet oxygen is not formed. The quartz surface on which the ions are adsorbed takes part in the formation of surface complexes which photosensitise the formation of singlet oxygen. When a bulk oxide phase is produced, these complexes are not formed,[14] and singlet oxygen is not generated.

Thus the carrier influences the nature and state of the sensitiser, and this may be revealed by a change in the nature of the deactivation of its excited states. In addition, dimerisation or aggregation of the sensitiser and modification of its electronic structure by the adsorbent are possible. All this must be taken into account in the study of the photosensitised formation and emission of singlet oxygen into the gas phase in heterogeneous solid–gas systems.

The nature of the solid may also influence the formation and emission of singlet oxygen into the gas phase. Thus the formation of singlet oxygen has been studied in experiments in which the support for the sensitiser (trypaflavine) was zinc oxide, whose electronic properties could be altered.[84] The formation and emission of singlet oxygen into the gas phase was observed only after extensive oxidation of ZnO. After the reduction of the oxidised zinc oxide in the course of the experiment, the formation of singlet oxygen stopped. This result can be understood if account is taken of the effect of the spectral sensitisation by dyes of the photoconductivity of zinc oxide.[60] When oxygen is adsorbed on the surface of zinc oxide, thermally activated capture of electrons takes place on the surface levels of the adsorbed oxygen. According to Ref.85, it is on these levels that effective transfer of the excitation energy of the adsorbed sensitiser takes place. In reduced ZnO, the concentration of surface ionised zinc is high.[86] When oxygen is adsorbed, a high density of surface levels is created, and effective transfer of the excitation energy of the sensitiser (trypaflavine) to the support (zinc oxide) takes place. When ZnO is treated

with oxygen atoms (extensive oxidation), the quantity of surface superstoichiometric zinc atoms and the density of surface levels decrease sharply.[86] In this case the transfer of the excitation energy of the sensitiser to oxygen, that is the formation of singlet oxygen, becomes more effective.

In addition to the transfer of the energy of electronic excitation of the sensitiser to the solid, its vibrational degradation as a result of the interaction of the sensitiser molecule with the solid is also possible. The formation and emission of singlet oxygen into the gas phase with photosensitisation by a film of dye (trypaflavine) has been detected.[12,13] The dye molecules in the solid phase to a large extent retain their individual properties, since they are joined by weak dispersion forces.[60] A film of this kind can be regarded as a strongly absorbing surface layer on a support. It is apparently these characteristic features of the behaviour of the dye molecule in the solid phase that determine the regular features of the formation and emission of singlet oxygen into the gas phase. A hundred-fold increase in the rate constant for the degradation of the energy of the triplet excitation of the sensitiser compared with the adsorbed state has been detected.[84] This increase was related to the vibrational degradation of the excitation energy of the sensitiser as a result of reaction with the support. Thus in the study of the regular features of the formation and emission of singlet oxygen into the gas phase in heterogeneous solid–sensitiser–oxygen systems it is necessary to take account of the distribution of the excitation energy of the sensitiser between the solid and oxygen.

The dependence of the concentration of singlet oxygen in the gas phase on the oxygen pressure with sensitisation by adsorbed trypaflavine differs considerably for silica and quartz surfaces.[13] In the case of silica gel, the formation and emission of singlet oxygen into the gas phase is observed in a narrower range of oxygen pressures, and its maximum concentration is displaced to low pressures. This difference can be attributed to the effective deactivation of singlet oxygen in the pores of the silica gel. Thus the efficiency of sensitisers adsorbed on silica gel is low in photo-oxidation processes.

The influence of the adsorption characteristics of singlet oxygen on the efficiency of its formation and emission into the gas phase has not been studied, since there are no data on the adsorption of singlet oxygen.

The photosensitised formation of singlet oxygen when the role of the sensitiser is played by the solid is of considerable interest. Thus even in Ref.87 it was suggested that when zinc oxide with oxygen adsorbed on its surface is illuminated, the formation and emission of singlet oxygen into the gas phase should take place in the intrinsic absorption band. It has recently been suggested that singlet oxygen is formed in the photo-desorption of oxygen from zinc oxide[88] and in the photocatalytic osidation of hydrogen on potassium bromide.[89] No direct proof that singlet oxygen is formed was given, however.

In addition to the mechanism examined (it can be described as physical), which involves the transfer to oxygen, most probably adsorbed, of the energy of optical excitation by surface centres or adsorbed molecules, a chemical mechanism also exists. Its chief characteristic is the chemical reaction taking place on the surface to give singlet oxygen. Thus data have been obtained,[90] indicating that singlet oxygen is formed when a highly hydroxylated titanium dioxide surface is illuminated. The authors of the works cited, who had previously carried out extensive work on the photo-desorption of oxygen from the surface of $TiO_2$, found that when titanium dioxide, previously activated with chlorine and impregnated with a solution of caesium anthracene-9,10-bis(ethanesulphonate) (AES), which is an effective absorber of singlet oxygen, was illuminated, the quantity of oxygen desorbed was much smaller than in the absence of AES. It was concluded that in this system, singlet oxygen is formed on the $TiO_2$ surface. The mechanism of formation of $^1O_2$ includes: 1) the formation of $H_2O_2$ in the course of the photo-desorption of $O_2$ from the hydroxylated $TiO_2$ surface; 2) the oxidation of surface chloride ions to $ClO^-$ when $TiO_2$ is illuminated in an $O_2$ atmosphere; and 3) the reaction of surface $ClO^-$ ions with hydrogen peroxide:

$$ClO^- + H_2O_2 \rightarrow H_2O + Cl^- + {}^1O_2$$

Thus in this system the mechanism of formation of $^1O_2$ is chemical in character, like the homogeneous production of $^1O_2$ as a result of the reaction of $H_2O_2$ with the $ClO^-$ ion in solution.[91]

The liberation of singlet oxygen after heating a sensitiser previously irradiated with light at a low temperature has been observed.[92,93] Thus in Ref.93, alcoholic solutions of Rose Bengal and Methylene Blue were illuminated at −60 °C, and singlet oxygen was liberated after heating to room temperature. In Ref.92, illumination of polyvinylnaphthalene at 0 °C followed by heating without illumination to 30 °C also led to the emission of singlet oxygen. In the opinion of the authors cited, singlet oxygen is formed by the decomposition of peroxides stable at a low temperature, which in turn are produced as a result of the reaction of the substances inidcated with singlet oxygen. Thus accumulation of singlet oxygen, which is subsequently readily liberated, takes place.

Many questions have still to be answered. Thus it is not clear whether the singlet oxygen in heterogeneous systems is produced in the state $^1\Delta_g$ or $^1\Sigma_g^+$, there are no accurate data on the efficiency of its formation, the possible formation of singlet oxygen by reaction with singlet-excited molecules has not been studied, and a number of other problems, which have been successfully resolved for homogeneous systems, still remain.

The general character of the problems examined for the case of singlet oxygen has been demonstrated[94] in a study of the triplet–triplet transfer of energy from solid organic substances (naphthalene, 9,10-anthraquinone, etc.), excited by light, to molecules of the gas phase (penta-1,3-diene), leading to the *cis–trans* isomerisation of these molecules.

### 3. The Formation of Electronically Excited Oxygen Molecules as a Result of the Adsorption of Oxygen, Chemical Reactions, and Structural-chemical Transformations on Solid Surfaces

EPR has been used to study the reaction of oxygen with chromium ions deposited on silica gel, and the formation of the complex $[Cr^{5+}O_2]$ was detected.[159] The parameters of the EPR spectrum of this system agreed with the suggestion that the $O_2$ molecule in this complex is in the singlet-excited state. An analysis[161] of a large number of EPR studies of complexes of $O_2^-$ radical-ions with $Ti^{4+}$ and $V^{5+}$ ions showed that the ground state of molecular oxygen in the coordination sphere of these metals must be singlet.

The adsorption of oxygen on the (100) and (110) faces of a single crystal of copper has been studied.[160] Ultraviolet photoelectron spectroscopy identified several forms of adsorbed oxygen, including a molecular form, stable at temperatures of 100–300 K, whose photo-electron spectrum consists of three bands. The authors cited consider that this form is an electronically excited $O_2$ molecule in the state $^1\Sigma_g^+$ (for the triplet $O_2$ molecule the photo-electron spectrum consists of five bands). This state of singlet oxygen, which is unstable in the gas phase, in the opinion of the authors cited is stabilised on the copper surface as a result of adsorption, and can react with various molecules.

The formation and emission into the gas phase of excited oxygen molecules can take place during the recombination of O atoms (a strongly exothermic reaction, $Q = 118$ kcal mole$^{-1}$) on solid surfaces. Thus it has been shown[76] that an appreciable proportion of the energy liberated in the recombination of oxygen atoms on metal surfaces is carried into the gas phase. The authors cited, however, do not indicate precisely in which energy state (vibrationally or electronically excited) the oxygen molecules leave the surface. In Ref.21 it was proved spectroscopically that electronically excited $^1O_2$ molecules are formed during the recombination of O atoms on nickel films. The authors cited consider that the production of an electronically excited $^1O_2$ molecule by the reaction:

$$NiO + O \rightarrow Ni + {}^1O_2 \quad (1)$$

is unlikely. The formation of the $^1O_2$ molecule in this system may take place by the reaction of an adsorbed O atom and an O atom leaving the gas phase:

$$NiO.O(ads) + O(gas) \rightarrow NiO + {}^1O_2 \quad (2)$$

Here, the excitation energy is determined by the dissociation energy of $O_2$ after subtraction of the energy of the bond formed by O(ads) with the NiO surface.

The emission of singlet oxygen as a result of the recombination of O atoms on Pyrex has been detected.[158] The probability of the formation of $^1O_2$ in this process is 0.2–0.4 (depending on the conditions of the experiment).

$^1O_2$ molecules can also be obtained as a result of the reaction of oxygen atoms with metal oxides. Mercury oxide has been studied in most detail in this connection. Even in early studies of the formation of singlet oxygen in electrical discharges in oxygen[19,20] it was noted that when the stream of active particles from the discharge passes over a film of mercury oxide there is a significant increase in the concentration of singlet oxygen in the gas phase, determined from the intensity of the spectral bands of $^1O_2$. The authors cited[20] consider that the singlet oxygen molecules are formed as a result of the reaction of oxygen atoms with mercury oxide.

In Ref.17, semiconducting detectors of singlet oxygen were used for the first time to study the emission of $^1O_2$ in this system. The O atoms were generated on a platinum filament and diffused to a film of HgO.

The dependence of the intensity of the signal of the detector (which was at room temperature) on the temperature of the thermal-decomposition filament was used to calculate the activation energy (53 kcal mole$^{-1}$) of this process, which was found to be approximately half the energy of rupture of the bond in the oxygen molecule. The result indicates that the magnitude of the signal in these experiments is proportional to the concentration of singlet oxygen, and that the emission of $^1O_2$ from the HgO surface is a reaction of first order with respect to oxygen. According to data on the change in the electrical conductivity of the detector, the ratio of the intensities of the fluxes of the O atoms falling on the HgO surface and the $^1O_2$ molecules leaving is close to 1, that is this reaction has a high efficiency.

The data obtained agree with the mechanism proposed in Ref.20:

$$HgO + O \rightarrow Hg + {}^1O_2 \quad (3)$$

The activation energy of reaction (3) is 5 kcal mole$^{-1}$, which is characteristic of processes involving oxygen atoms.[86]

As shown by Eqn.(3), the oxygen atoms reduce the mercury oxide surface, and this was observed visually from the darkening of the HgO film. As reduction proceeds, another process, competing with reaction (3), begins to play a larger role, namely the oxidation of the newly formed mercury atoms, leading to a decrease in the intensity of the flux of $^1O_2$ molecules from the HgO surface:

$$Hg + O \rightarrow HgO$$

During the experiment, the high initial intensity of the $^1O_2$ flux decreased regularly to a stationary value. Thus with a constant flux of primary active species, that is O atoms, the state of the HgO surface reflects redox reactions taking place simultaneously to establish a stationary flux of $^1O_2$ molecules into the volume.

Comparison of the results with published data[20,96] indicates that metal oxides whose surface layers can be even partially reduced by oxygen atoms (for example lead, silver, or mercury[96]) liberate $^1O_2$ molecules in the course of this reaction. This effect is observed because the energy of the bond formed by oxygen in the surface layer of, for example, PbO is half the standard enthalpy of formation of this oxide[97] and amounts to 40 kcal mole$^{-1}$. In other words, the emission of $^1O_2$ in reactions of this kind is possible only for those oxides whose surface oxygen atoms are relatively weakly bound in the crystal lattice.

Zav'yalov and Myasnikov[15] described for the first time a study of the formation and emission of singlet oxygen when a disordered quartz surface was heated in an oxygen atmosphere. In this case the energy necessary for the excitation and emission of the oxygen molecules is accumulated during the preliminary disordering of the surface layer of the solid, and is liberated during the relaxation of the disordered surface. It was discovered for the first time that singlet oxygen is liberated when quartz, freshly ground in oxygen (0.13 hPa) or in a vacuum, is heated in $O_2$. The temperature dependence of the intensity of the $^1O_2$ flux from the quartz surface in the range 200–600° is given by a curve with a maximum at 400 °C. The ascending branch of the curve corresponds to an intensification of the ordering of the structure of the surface layer (annealing of defects) with increase in temperature, and the descending branch is possibly related to a decrease in the concentration of defects in the surface layer of the adsorbent. It was noted that the emission of $^1O_2$ molecules is accompanied by a decrease in the intensity of the EPR signal, apparently as a result of the annealing of paramagnetic defects in the quartz. It is significant that the emission of $^1O_2$ molecules was not observed on fused quartz (which does not contain surface paramagnetic defects).

On isothermal heating, the rate of the liberation of singlet oxygen gradually decreases, and the kinetics of this process do not obey the equation for a unimolecular reaction. Thus the formation and emission of singlet oxygen molecules from the quartz surface are more complex than the simple decomposition of surface compounds with the liberation of $^1O_2$ into the gas phase, and are apparently determined by the annihilation of defects in the quartz layers next to the surface in the presence of $O_2$.

Another method can also be used to activate a quartz surface with respect to $^1O_2$ emission. In Ref.98 it was discovered that when a quartz vessel in which a stoichiometric $H_2 + O_2$ mixture had previously been exploded was heated under programmed conditions to temperatures of 400–500 °C at an $O_2$ pressure of 0.13 hPa, emission of singlet oxygen into the gas phase begins. The temperature dependence of the emission of $^1O_2$ in this case is similar to that for the surface of ground quartz. Thus for quartz surfaces "perturbed" in different ways, the relaxation of the disordering of the surface layers in the presence of $O_2$ is accompanied by the production of singlet oxygen. The result is also of interest in relation to the participation of the walls of a reaction vessel in the production and emission of excited species in chain processes taking place at low pressures.

The conditions of the formation and emission of singlet oxygen from the surface of an Li–Sn–P catalyst have been studied.[16] When oxygen (4 hPa) or air is blown through a U-shaped quartz reaction vessel containing tablets of an oxide catalyst (58.4% Sn, 10% P, and 1.5% Li), heated to 650 °C, singlet oxygen is liberated into the volume, as established from the change in the concentration of a solution of rubrene in hexadecane, placed in a cell separated from the reaction vessel (rubrene is a specific reagent for singlet oxygen[7]). More than 20 oxide catalysts were studied. The intensity of the emission of singlet oxygen from the catalyst surface was estimated from the degree of transformation of rubrene 1 h after the start of the experiment. This quantity was 30–50% for the lithium–tin–phosphate catalysts, and 1% in the absence of lithium, as in the case of manganese and cobalt oxides.

The rate of the liberation of $^1O_2$ increased with increase in temperature. The duration of the emission was 4 h. The process did not stop when oxygen was replaced by argon. The authors cited concluded that this indicates that $^1O_2$ is formed with the participation of surface oxygen on centres which break down in the course of the reaction or on the decomposition of unknown impurities in the catalyst. It is suggested that lithium in this system is converted into the superoxide, facilitating the generation of singlet oxygen. Singlet oxygen was not liberated when other catalysts, ZnO, $Ag/Al_2O_3$, $CaO/Al_2O_3$, $Cr_2O_3/Al_2O_3$, etc. were heated.

The emission of singlet oxygen from the surface of vanadium pentoxide, a widely encountered oxidation catalyst, has been observed.[23] $^1O_2$ molecules are emitted into the gas phase when $V_2O_5$ powder is heated in an atmosphere of ordinary oxygen to 300–500 °C. The initial intensity of the liberation of $^1O_2$ increases with increase in temperature. At a constant $O_2$ pressure (0.13 hPa) and a constant temperature, the emission of $^1O_2$ continues for several hours. The activity of the catalyst is restored after heating in $O_2$ at a temperature of 600 °C and atmospheric pressure. In contrast to the experiments at low $O_2$ pressures, the intensity of the $^1O_2$ flux remains unchanged with time at atmospheric pressure. From this the authors cited conclude that the emission of singlet oxygen from the $V_2O_5$ surface may be due to reversible structural-chemical transformations in the catalyst, taking place at high $O_2$ pressures and high temperatures. The observation that continuous emission of $^1O_2$ from a $V_2O_5$ surface takes place at atmospheric pressure of oxygen is important for an understanding of the mechanism of stationary oxidation reactions on this catalyst.

This is confirmed by the results of a comparison[99] of the regular features of the emission of singlet oxygen from a vanadium pentoxide surface and the oxidation of naphthalene on the same catalyst. The intensities of the two processes (the emission of $^1O_2$ and the formation of phthalic anhydride) changed in the same sense with change in the conditions of the experiments (treatment of the catalyst with the reaction mixture, heating in a vacuum, etc.). It was also established that naphthaquinone, one of the intermediate products of the oxidation of naphthalene, is formed at a low concentration of singlet oxygen. Thus the participation of singlet oxygen in the heterogeneous catalytic oxidation of organic substances was proved experimentally for the first time for the case of the oxidation of naphthalene to phthalic anhydride on a vanadium catalyst. These data indicate that singlet oxygen plays an important role in oxidation processes taking place by both heterogeneous and heterogeneous–homogeneous mechanisms.

Finally, it is appropriate to draw certain conclusions about the regular features of the emission of singlet oxygen from solid surfaces into the gas phase. The improvement of old methods for detecting singlet oxygen and the development of new methods, in particular the use of semiconducting $^1O_2$ detectors,[17,51] have made it possible to extend considerably the range of the study of physico-chemical processes leading to the formation and emission of singlet oxygen and to establish various characteristic features of their mechanism. In all cases, singlet oxygen is formed as a result of the transfer of excitation energy from a solid or an adsorbed layer to oxygen molecules. The source of this energy may be light (photochemical reactions), the energy of the recombination or reaction of atomic oxygen with metal oxides (chemical reactions), thermal energy (the decomposition of various metal oxides), or energy liberated in the disordered surface layers of a solid during their ordering (structural-chemical processes). All this indicates that it is highly probable that singlet oxygen also appears in other processes in which a solid is excited in the presence of oxygen, for example under the influence of electrons, ions, radiation of different kinds, and in general as a result of reactions leading to marked and reversible breakdown of the structure of the surface layers of solids.

Particular mention may be made of the as yet limited data[159–161] on the possible formation of singlet oxygen on the surface of solids as a result of the adsorption of $O_2$. An early suggestion,[162] subsequently discussed repeatedly,[1,163] proposed that the surface compounds formed on the chemisorption of molecules could be regarded as electronically excited states of these molecules. This idea has been confirmed for the case of $^1O_2$. In a number of cases, marked perturbation of the adsorbed oxygen molecules takes place, and the singlet-excited state of $O_2$ is produced. Thus in the case of oxygen there is apparently an analogy between the properties of electronically excited and surface-coordinated molecules.

## 4. The Formation and Emission of Electronically Excited Metal Atoms and Nitrogen Molecules from Solid Surfaces

There are few published data on the emission of electronically excited nitrogen molecules from solid surfaces.

A number of papers by Mannella and co-workers,[100–102] published in the nineteen-sixties, described the luminescence of the surfaces of cobalt and nickel during the simultaneous recombination of nitrogen and oxygen atoms. The experiments were carried out in a flow system at a pressure of 1.3 hPa. The stream of nitrogen and oxygen atoms, obtained in a discharge, was passed over the surface of metallic nickel or cobalt inserts embedded in a glass tube. The luminescence of the gas was recorded at the outlet from the reaction zone. The luminescence spectra in the case of cobalt showed the first positive bands of nitrogen. The authors cited consider that electronically excited $N_2(B^3\Pi_g)$ molecules, with an excess of vibrational energy ($v = 6, 8$), are formed on the cobalt surface and are desorbed into the gas phase, where they emit light as a result of the transition:

$$N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+) + h\nu$$

In the case of nickel, the luminescence spectrum of the gas shows both the first positive bands of nitrogen and the β-bands of nitric oxide. The authors cited suggested that the species desorbed from the nickel surface are electronically excited $NO(B^2\Pi)$ molecules, which subsequently either lose energy:

$$NO(B^2\Pi) \rightarrow NO(X^2\Pi) + h\nu \ (\beta\text{-band of NO})$$

or react with nitrogen atoms:

$$NO(B^2\Pi) + N(^4S) \rightarrow N_2(B^3\Pi_g) + O(^3P)$$

$$N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+) + h\nu \ (\text{first positive band of nitrogen})$$

In Ref. 102, the luminescence of $N_2^*$ molecules above a nickel surface was observed only in the presence of O atoms.

The emission of various electronically excited atoms and molecules from solid surfaces also takes place as a result of electron bombardment. The extensive literature on electronically stimulated desorption (ESD) includes recent papers on the ESD of excited species. The ESD of excited Na, K, and Li atoms from NaCl, KCl, and LiF surfaces has been studied.[103,104,164] The intensity ($I$) of the resonance emission of the excited atoms was measured, and the dependence of $I$ on the energy ($E$) of the electron beam (20–1000 eV) determined. The $I = f(E)$ curves for NaCl showed characteristic features which correlate with the energies of the electron levels of Na and Cl ions in the halide lattice. For example, for Na the luminescence appearance threshold (32 eV) is close to the 2$p$ level of Na (31 eV), and the increase in $I$ at 65 eV is associated with the 2$s$ level of Na (63 eV). The fine structure at 200 eV on the $I = f(E)$ curve corresponds to the 2$p$ level of Cl (200 eV and 202 eV). A mechanism was proposed for the ESD of Na*, according to which $Na^{2+}$ ions are formed in the first stage. Subsequently, an Auger process produces $Na^+$ ions, which pass through the matrix next to the $Cl^-$ ions in the surface layer and are neutralised with the formation of a resonance excited Na* atom. The radiative deactivation of Na* takes place beyond the NaCl surface.

A characteristic feature is that the excitation of the Na, K, and Li atoms takes place on the surface of the crystals, and not in the gas volume. This conclusion is based on the following facts: 1) the vapour pressure of the metals, determined by the temperature of the surface in the electron emission zone, is too low, and 2) slight displacement of the crystal target from the direction of the electron beam leads to disappearance of the effect.

The authors cited also found that excited hydrogen atoms and hydroxyl radicals are emitted in addition to metal atoms.

An energy analysis of the ESD relationships for excited alkali metal atoms[165] established that the transfer of the energy of the electrons takes place as a result of the formation of holes in the inner levels of the atoms. In subsequent stages, various electronic processes produce excited metal atoms, which are ejected from the surface. A characteristic feature is that the atoms are desorbed in the first (lowest) excited state.

The ESD of excited atoms and ions from different surfaces was described in Refs. 166–168. When a glass surface was irradiated with an electron beam (300 eV) at low cadmium vapour pressures ($10^{-3}$ hPa), emission of excited cadmium ions took place, detected by the luminescence at 441.6 nm and 537.8 nm.[166] The same authors[167] previously detected the emission of excited cadmium ions from the surface of silvered copper.

Mass spectrometry has been used[168] to study the ESD of hydrogen ions and atoms from an Ni (111) surface covered with a film of water. It was found that at an electron energy of 22–30 eV, $H^+$ ions are ejected into the volume, whereas at 35 eV, electronically excited metastable H atoms in the (2$s$) state are ejected. It is emphasised that the metastable hydrogen atoms are not formed from $H^+$ ions, since the energy of the ejected H atoms is 4–5 eV higher than the energy of the desorbed $H^+$ ions.

Finally, emission in an electronically excited state takes place during the ionic sputtering of materials. Charged and neutral species in different states are formed on the surface and ejected into the gas phase.

Data on the emission of the species produced when solid surfaces are bombarded by inert gas or hydrogen ions with energies from 1 to thousands of eV have been reviewed.[169] Spectroscopic methods have been used to detect the excited species formed in various processes: 1) the scattering of the excited state of the atoms of the primary beam; 2) the emission from the excited state of atoms, molecules, or complexes formed from the atoms of the target; and 3) the formation of excited states of adsorbed molecules. The materials studied were mainly metals, and some metal oxides.[170] The mechanism of the emission by excited atoms and ions has recently been studied using a new spectroscopic method, involving the measurement of the Doppler shift of the fluorescent atoms ejected from metal surfaces during ionic sputtering (the fluorescence is excited by a laser light beam). For example, the yields and velocity distribution of sputtered barium atoms in the ground and metastable states Ba($^1S$) and Ba($^1D$) have been measured, and the influence of oxygen on these characteristics studied.[171] In Ref. 172, a similar study was carried out using metastable Fe* atoms sputtered from an iron surface. Studies in this field are developing rapidly.

The reported observation[173] of the formation of excited Na atoms on an NaCl surface during the recombination of deuterium atoms is of interest. On thin films of NaCl, for which the coefficient of the heterogeneous recombination of D atoms is high, the spectrum of the luminescence observed corresponds to the D line of sodium atoms. It is not clear, however, whether emission of Na* atoms takes place in this case.

Overall, it appears that published data on the emission of excited metal atoms deal only with the cases of the "strong" perturbation of solid surfaces by electron or ion bombardment. There are practically no published data on the emission of these species under "mild" conditions (chemical and structural-chemical processes, ultraviolet irradiation, etc.).

## III. THE DEACTIVATION OF ELECTRONICALLY EXCITED ATOMS AND MOLECULES ON A SOLID SURFACE

In the reaction of electronically excited atoms and molecules with a solid surface, their deactivation can take place by the following paths: 1) relaxation of the excited state as a result of the dissipation of the excitation energy in the adsorbed layer and in the surface layers of the solid, which may involve both phonons and the electronic sub-structure of the crystal; 2) chemical reaction with atoms of the surface or the adsorbed layer; and 3) luminescence of electronically excited molecules in the adsorbed layer.

From a comparison of the values of the coefficients of the heterogeneous deactivation $\gamma$ of electronically excited atoms and molecules (the terms deactivation, relaxation, or accommodation coefficient are also used), it is difficult to decide which deactivation channel predominates, since the value of $\gamma$ gives a representation of the overall activity of different materials with respect to their reaction with excited species.

As shown below, in a number of cases it is possible to reach a conclusion about the mechanism of deactivation from the dependence of the value of $\gamma$ on the conditions of the experiment, which alter the properties of the solid which are "sensitive" to the transfer of the energy of the excited atoms and moelcules. There have been practically no studies of the microscopic mechanism of the heterogeneous deactivation of electronically excited molecules.

Data have been published on the reactions of various solid surfaces with singlet oxygen, metastable inert gas atoms and nitrogen molecules, and triplet molecules of organic substances.

## 1. Electronically Excited Oxygen Molecules

The heterogeneous deactivation of singlet oxygen has been studied in most detail. It is appropriate to examine three classes of surface differing in their activity with respect to the deactivation of $^1O_2$ ($^1\Delta_g$) molecules: dielectrics ($\gamma = 10^{-5}-10^{-3}$), metal oxides ($\gamma = 10^{-4}-1$), and metals ($\gamma = 10^{-5}-1$).

Most values of $\gamma$ on glass and quartz surfaces have been obtained by studying the gas-phase reactions of singlet oxygen, since the reaction vessels are usually made of these materials. The studies are usually carried out in a flow apparatus, and the singlet oxygen is obtained by a discharge in oxygen. This procedure has a number of significant unsatisfactory features: firstly, in a flow apparatus it is difficult to achieve the necessary cleanliness of the surface, since lubricant vapour is present, contamination from the gas phase is possible, etc.; secondly, in the generation of singlet oxygen in a discharge there are active products (oxygen atoms, ozone, etc.), which modify the surface. Moreover, at a high concentration of singlet oxygen the surface may again be modified, and this should lead to a change in the heterogeneous deactivation coefficient. For example, in Refs.106–109, 118, and 158, the coefficient of the deactivation of singlet oxygen on Pyrex varied from $7.6 \times 10^{-6}$ to $5 \times 10^{-5}$. These results show convincingly that the magnitude of the coefficient of the heterogeneous deactivation of singlet oxygen is influenced considerably by the conditions of the experiment. This conclusion is confirmed by studies[2,140] in which a change in $\gamma$ in the course of the experiment was observed, indicating that the surface is modified during the measurements. In Ref.105, the value of $\gamma$ on silicon increased slowly with time. In the works cited, no mechanism was proposed for the deactivation of singlet oxygen, and all the values were obtained only for room temperature.

Thus to investigate the mechanism of the deactivation of singlet oxygen on a solid surface, it is necessary to carry out studies under clean conditions (high vacuum, absence of surface contaminants, a selective source of singlet oxygen) and at low concentrations of singlet oxygen.

Attempts have been made to satisfy these conditions.[112] The experiments were carried out under diffusion conditions, and the surface was treated by heating at 250–300 °C in a high vacuum ($10^{-7}$ hPa), achieved using oil-free magnetic-discharge and zeolite pumps. Singlet oxygen was obtained by photosensitisation by an adsorbed dye (trypaflavine). The gas phase did not contain any other active species. The concentration of singlet oxygen in the gas phase ($10^{10}$ cm$^{-3}$) was measured using semiconducting detectors. With increase in the temperature of the surface, the deactivation coefficient of singlet oxygen on glass decreases, and at 373 K is equal to $10^{-6}$ ($\gamma = 10^{-5}$ at 293 K). The activation energy of the change in $\gamma$ is negative and equal to 6 kcal mole$^{-1}$. $\gamma$ is independent of the oxygen pressure in the range $1-10^{-2}$ hPa. These data indicate that on a glass surface, singlet oxygen is deactivated as a result of physical adsorption with subsequent transfer of energy to the solid; this process is analogous to the relaxation of vibrationally excited nitrogen molecules on silver and Teflon at low temperatures.[111] The mechanism of the deactivation corresponds to the following scheme:

$$^1O_2 + Z \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} {}^1O_2Z$$

$$^1O_2Z \xrightarrow{k_2} {}^3O_2Z$$

where $Z$ is an adsorption centre.

If the rate of deactivation of $^1O_2$ is much lower than the rate of desorption ($k_2 \ll k_{-1}$), the adsorption of singlet oxygen on the surface can be regarded as a quasi-equilibrium process, and described by the Langmuir isotherm. Since the concentration of singlet oxygen is low, it can be assumed that the adsorption takes place in the Henry range. Thus

$$\gamma = \frac{4k_H k_2 kT}{\bar{v}} \frac{S}{V}$$

where $k_H$ is the Henry constant, $S$ the surface area, $V$ the volume, $k$ the Boltzmann constant, $P$ the temperature, and $\bar{v}$ the average velocity of the particles.

The scheme describes the experimental results satisfactorily. The activation energy for the change in $\gamma$ in this case is equal to the heat of adsorption of singlet oxygen on the glass surface.

The Henry constant can be estimated by the method of Zweitering and Krevelen:[141]

$$k_H = \frac{N_A}{(2\pi MRT)^{1/2}} \tau_0 \exp(Q/RT)$$

where $N_A$ is Avogadro's number, $M$ the molecular mass of the gas, $R$ the gas constant, $\tau_0$ the period of one vibration of the adsorbed molecule in a direction perpendicular to the surface, and $Q$ the heat of adsorption.

The measured coefficient of the heterogeneous deactivation of the species ($10^{-5}$ at room temperature) and the heat of adsorption (6 kcal mole$^{-1}$) can be used to estimate the relaxation time of the energy of singlet oxygen on the glass surface:

$$\tau_{rel} = k_3^{-1} = \frac{4k_H kT}{\gamma \bar{v}} = \gamma^{-1}\tau_0 \exp(Q/RT)$$

For $\tau_0 = 10^{-12}-10^{-13}$ s, $\tau_{rel} = 10^{-3}-10^{-4}$ s. This value is very much higher than the relaxation time of vibrationally excited nitrogen molecules on glass ($10^{-8}$ s),[111] apparently because of the difficulty of the relaxation of the comparatively high energy (1 eV) on the surface.

In Ref.89, the relaxation time of singlet oxygen on a KBr surface was found to be greater than $10^{-2}$ s. In Refs.110 and 142, the factors influencing the heterogeneous deactivation of singlet oxygen were investigated by another method. The temperature dependence of the coefficient of the heterogeneous deactivation of singlet oxygen on quartz was determined by the standard method (flow system, $^1O_2$ produced by an ultrahigh-frequency discharge in oxygen) at temperatures of 350–900 K. In addition, the surface was modified by the adsorption of gases, as in Refs.143 and 150. The value of $\gamma$ was measured by estimating the degree of deactivation of $^1O_2$ on a quartz rod introduced into the reaction vessel or directly on the walls of the cylindrical quartz reaction vessel. In the first case, in the temperature range 520–830 K at an $O_2$ pressure of 0.6 hPa, $\gamma = (7.4 \pm 0.5) \times 10^{-3}\exp(18.5 \pm 1.0/RT)$, where the activation energy is given in kJ mole$^{-1}$. In the second case, with increase in temperature from 350 K to 600 K, $\gamma$ increases from $1.1 \times 10^{-4}$ to $1.8 \times 10^{-3}$ (the activation energy is 18.5 kJ mole$^{-1}$), but with further increase in temperature it remains unchanged up to 900 K. The values of $\gamma$ differ by a factor of approximately 10, apparently due to a difference in the concentration of deactivation centres. Under the chosen conditions, the value of $\gamma$ was independent of the oxygen pressure. When $H_2O$, $NH_3$, or oxygen atoms were added to the stream of oxygen, the concentration of $^1O_2$ increased, indicating a decrease in the deactivation of $^1O_2$. The addition of Ar, $H_2$, CO, or $C_2H_4$ had little influence on the deactivation. These data confirm the chemisorption mechanism of the deactivation of $^1O_2$ on the surface centres of quartz. When the quartz has been heated, the number of free centres increases (and $\gamma$

increases), and when active gases are introduced, the centres are blocked ($\gamma$ decreases). The nature of these centres has not yet been determined. The authors cited[110,142] consider that these centres may be radical peroxide forms of oxygen.

After the adsorption of benzene on the glass surface, $\gamma$ was found to be $4 \times 10^{-5}$.[143]

When all the material on the deactivation of $^1O_2$ on quartz and glass surfaces is reviewed, it is possible to make some generalisations. At temperatures close to room temperature, the deactivation coefficient is $10^{-5}$, and the deactivation mechanism apparently involves the physical adsorption of $^1O_2$. At higher temperatures and concentrations of singlet oxygen, deactivation takes place by a chemisorption mechanism. The nature of the adsorption centres and the mechanism of the relaxation of the energy of $^1O_2$ on the glass surface is still not clear.

The deactivation of singlet oxygen on the surface of metal oxides has been studied for the case of zinc and oxide.[112] With increase in temperature, the value of $\gamma$ increased from $10^{-4}$ to $10^{-2}$, and the activation energy of the change in $\gamma$ was 25 kcal mole$^{-1}$. $\gamma$ decreased with increase in the oxygen pressure (in the range $5 \times 10^{-2}$–2 hPa). It was suggested that in this case the deactivation of singlet oxygen takes place as a result of its chemisorption on the zinc oxide surface:

$$^1O_2 + Z \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} {}^1O_2Z$$

$$^3O_2 + Z \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} {}^3O_2Z$$

$$^1O_2Z \xrightarrow{k_5} {}^3O_2Z$$

where $Z$ is an adsorption centre.

According to this scheme, the loss of the energy of electronic excitation is due to the formation of a chemical bond, that is chemisorption. If the residence time of the singlet oxygen molecule in the adsorbed state is greater than the time for the loss of the excitation energy, that is $k_{-3} \ll k_5$, then in accordance with the method of stationary concentrations it is possible to write:

$$\gamma = \frac{s_1}{s_1[^1O_2]/[^3O_2] + s_2} \cdot \frac{4k_{-4}[Z]}{\bar{v}[^3O_2]} \qquad (5)$$

where $s_1$ and $s_2$ are the adhesion coefficients of $^1O_2$ and $^3O_2$, and $\bar{v}$ the average velocity of the particles. It follows from Eqn.(5) that $\gamma$ should decrease with increase in pressure, in agreement with the experimental data. The temperature dependence of $\gamma$ is determined by the rate constant of the desorption of $O_2$ from the zinc oxide surface (that is $k_{-4}$). Increase in temperature leads to an increase in the number of free centres for the chemisorption of $^1O_2$, and $\gamma$ increases. The measured value of the activation energy of the change in $\gamma$ (25 kcal mole$^{-1}$) agrees with published data for the activation energy of the desorption of oxygen from a ZnO surface (23 kcal mole$^{-1}$).[114] Under the conditions of the experiment, equilibrium chemisorption of oxygen on the zinc oxide surface is achieved, since $\gamma$ changes little with time. The nature of the centres for the chemisorption of singlet oxygen is of considerable interest. Thus the electrical conductivity of a film of zinc oxide decreases under the influence of $^1O_2$.[17] The decrease in the concentration of conductivity electrons may take place as a result of the formation of a chemical bond between a singlet oxygen molecule and a superstoichiometric ionised surface zinc atom. In this case the coefficient of the heterogeneous deactivation of singlet oxygen on the zinc oxide surface should decrease with decrease in the concentration of zinc atoms, as observed experimentally.

In the reaction of electronically excited molecules, which are chemically inert with respect to zinc oxide (for example the triplet molecules of benzophenone or diacetyl and excited inert gas atoms), the excitation energy of the molecules is transferred to the layer of zinc oxide next to the surface, and the electrical conductivity of the film increases.[144,145] If the surface of the zinc oxide film is deactivated with respect to the chemical action of singlet oxygen, that is if the concentration of zinc atoms acting as chemisorption centres is decreased considerably, a similar effect should be observed. In fact, it has been found[113] that when a source of $^1O_2$ (an ultrahigh-frequency discharge, a photochemical source, or the reaction HgO + O) is included, the electrical conductivity $\sigma$ of the film at the initial moment increases, passes through a maximum, and then decreases. The result can be understood if it is assumed that in the reaction of $^1O_2$ with the ZnO film, two processes take place simultaneously (but at different rates), one of which (the more rapid) is associated with the transfer of the energy of the $^1O_2$ molecule to zinc oxide and hence with an increase in $\sigma$, while the other (the slower) is associated with the chemisorption of $^1O_2$ on the zinc atom impurity centres responsible for the impurity conductivity of ZnO. The extremal character of the change in $\sigma$ is attributed to the competition between these two processes. This system is characterised by chemical deactivation of $^1O_2$. These experiments lead to certain conclusions about the mechanism of the transfer of the excitation energy of singlet oxygen in ZnO. The existence of the donor signal of the change in the electrical conductivity $\sigma$ on the adsorption of $^1O_2$,[113] which was also observed in the reaction of $^1O_2$ with a single crystal of ZnO in a solution of electrolytes,[146] indicates that the excitation energy is transferred to the surface layers of ZnO and brings about the ionisation of fine traps and the ejection of electrons into the conductivity band. The same results were obtained in experiments with zinc oxide photo-currents photosensitised by dyes.[85] Two mechanisms of the photosensitisation have been discussed. One assumes that the excitation energy is transferred to the semiconductor, and the other that the excited dye is ionised. When singlet oxygen is adsorbed on the surface of the semiconductor, the second mechanism is unlikely, since it is difficult to imagine the formation of positive oxygen ions.

There are few published data on the reaction of $^1O_2$ with other metal oxides. The adsorption of $^1O_2$ on magnesium, nickel, and cobalt oxides has been studied.[147,148] On MgO there is weak adsorption of $^1O_2$, which decreases with increase in temperature from −78 °C to 20 °C (the adsorption of ordinary triplet oxygen on MgO increases with increase in temperature). The adsorption of $^1O_2$ on NiO takes place with a greater intensity than on MgO, and is independent of temperature. In the case of $Co_3O_4$, no differences in the adsorption of singlet and triplet oxygen could be observed. The authors cited did not examine the mechanism of the reaction of $^1O_2$ with the oxides. On the surface of cobalt oxides, the coefficient of the heterogeneous deactivation of $^1O_2$ is high (~1).[152] This property has been made the basis of a calorimetric method for measuring the concentration of $^1O_2$. The mechanism of the reaction of singlet oxygen with cobalt oxides is not clear. The strong heating of the $Co_3O_4$ film may be due not only to a thermal mechanism of deactivation but also possibly to a chemisorption mechanism, involving the heat of chemisorption.

The heterogeneous deactivation of singlet oxygen on a dye surface (trypaflavine) has been studied.[66] With increase in temperature from 293 K to 343 K, $\gamma$ increases from $10^{-3}$ to $10^{-2}$. The same dependence of $\gamma$ on the $O_2$ pressure was observed for zinc oxide, so that the deactivation of singlet oxygen takes place by a chemisorption mechanism, and the

activation energy of the change in $\gamma$ is the activation energy of the desorption of oxygen from the dye surface.

The heterogeneous deactivation of $^1O_2$ on metal surfaces has been the subject of a number of studies. The concentration of $^1O_2$ was measured from the singlet oxygen luminescence. The experiments were carried out at pressures of from tenths to several hPa, in a flow system. The following values of $\gamma$ were obtained at room temperature:[105] Al ($5.9 \times 10^{-5}$), Ti ($6.5 \times 10^{-5}$), Mo ($8.0 \times 10^{-5}$), Nb ($1.2 \times 10^{-4}$), Pt ($4.0 \times 10^{-4}$), Cu ($8.5 \times 10^{-4}$), Ni ($2.7 \times 10^{-3}$), Fe ($4.4 \times 10^{-3}$), and Ag ($1.1 \times 10^{-2}$). The results of the measurements for Ag, Pt, and Al agree with the data obtained by other authors, for example in Ref.115. On a stainless steel surface, $\gamma$ varied from $7.6 \times 10^{-6}$ to $1.3 \times 10^{-5}$ at room temperature.[149] The coefficient of the heterogeneous deactivation of singlet oxygen on a gold surface with previously adsorbed HCl is $(1-3) \times 10^{-3}$.[150] On an annealed Au specimen, the value of $\gamma$ changed from $5 \times 10^{-2}$ to $2 \times 10^{-1}$ in the temperature range 300–900 K. The adsorption of water at 300 K led to a decrease in $\gamma$ by a factor of 20.[142,151] In the opinion of the authors cited, these results confirm that the deactivation of $^1O_2$ on an Au surface takes place by a chemisorption mechanism:

$$AuO + O_2(^1\Delta_g) \rightarrow AuO{-}O_2(^1\Delta_g) \rightarrow AuO + O_2(^3\Sigma_g^-)$$

It was suggested that the bond formed by the chemisorbed $^1O_2$ with gold oxide is strong, and that its energy is transferred to some degrees of freedom of the metal. Ordinary oxygen is not chemisorbed on these centres, and is readily liberated into the gas phase. By analogy with the gas-phase reactions of excited species, the proposed mechanism was described as an excimer mechanism. On a strongly hydroxylated gold surface, the chemisorption of $^1O_2$ is impossible, the value of $\gamma$ is much lower, and the deactivation mechanism is different.

Other regular features were observed for platinum. On the surface of a Pt wire, $\gamma$ increases from $10^{-3}$ to $10^{-1}$ with increase in temperature from 300 K to 450 K. The value of $\gamma$ is almost independent of the $O_2$ pressure in the range 0.17–6.0 hPa. The effective activation energy decreases with increase in temperature, from 46.5 kJ mole$^{-1}$ at 300 K to 0 at 450 K. The addition of water and hydrogen does not influence the rate of the deactivation of $^1O_2$, but the introduction of CO (7%) decreases $\gamma$ at 400 K by a factor of ten. The authors cited consider that these results are consistent with a chemisorption mechanism. The increase in $\gamma$ with temperature was related to an increase in the number of active centres on the surface, and the limiting stage is the adsorption of singlet oxygen on the free centres. These centres may be various forms of adsorbed oxygen. The action of CO involves either the blocking of these forms of oxygen or their removal from the surface as a result of a chemical reaction.

The value of $\gamma$ for nickel was found to be close to 1.[157]

Thus on metal surfaces the values of the coefficients of the heterogeneous deactivation of $^1O_2$ differ by several powers of ten, from $10^{-5}$ for Al to 1 for nickel. It should be noted that these values relate rather to the oxidised surface of the metals, since the measurements were made under fairly "severe" conditions (a high concentration of $^1O_2$ in a stream of oxygen). The results of the measurements depend on the conditions of the evacuation and the treatment of the specimens, particularly at high temperatures, and also on the composition of the adsorption layer. Thus in the discussion of a particular value of $\gamma$ it is necessary to specify clearly the conditions of the experiments. There are few published data on the heterogeneous deactivation of the $^1O_2$ molecule in the state ($^1\Sigma_g^+$). The deactivation coefficient of this species was determined by measuring the intensity of the 7618 Å line in a stream of oxygen, passed through a discharge and mercury oxide, after reaction with a metal insert. According to Ref.115, for $^1O_2(^1\Sigma_g^+)$, $\gamma$ has the values 0.3 (Fe), 0.25 (Al), 0.9 (Cu), 0.6 (Ag on Pt), and ~0 for pure Pt. Thus on all these metals (except Pt) the deactivation coefficient is very high. For a glass surface, the following values of $\gamma$ were obtained: $10^{-3}-10^{-2}$,[116] $1.5 \times 10^{-2}$,[117] $0.9 \times 10^{-2}$,[118] $10^{-2}$,[119] and $2 \times 10^{-2}$.[107] The average value of the deactivation coefficient of $^1O_2(^1\Sigma_g^+)$ on glass is $10^{-2}$, which is $10^3$ times that for the state ($^1\Delta_g$). The lowest value of $\gamma$ was obtained for a glass surface covered with a halocarbon lubricant, $1.1 \times 10^{-3}$.[154] The shrot lifetime and the high efficiency of the deactivation of $^1O_2(^1\Sigma_g^+)$ are the chief reasons for the considerable experimental difficulty of measuring $\gamma$, and this explains why few papers on this topic have been published. The published data indicate that the efficiency of the deactivation of singlet oxygen depends markedly on the excitation energy. The deactivation coefficient is higher (by a factor of $10^2-10^3$) for the ($^1\Sigma_g^+$) state which has a higher energy than $O_2(^1\Delta_g)$, and this is related to the high efficiency of the conversion of the state ($^1\Sigma_g^+$) into ($^1\Delta_g$) on collision with the surface, and probably to the high chemical activity of the state ($^1\Sigma_g^+$). For oxygen in the $A\,^3\Sigma_u^+$ state with even higher energy, the deactivation coefficient on glass is ~1.[153]

In spite of the progress made in the study of the mechanisms of the deactivation of singlet oxygen on solid surfaces, all the studies discussed above have a significant unsatisfactory feature. In these studies the state of the surface was not examined by structure-sensitive methods, and this is necessary in the determination of the singlet oxygen adsorption centres.

### 2. Metastable Inert Gas and Mercury Atoms and Nitrogen Molecules

The heterogeneous deactivation of the metastable atoms of inert gases (MAIG) on metal surfaces is accompanied by secondary electron emission (SEE). There are two SEE mechanisms:[120,121] a two-stage mechanism based on the resonance ionisation (RI) of an incident excited atom, followed by Auger neutralisation (AN) of the ion formed, and a single-stage mechanism involving Auger deactivation (AD).

The mechanism predominating is determined by the position of the excitation level of the incident atom relative to the Fermi level of the metal, and by the ratio of the work function of the electron and the ionisation potential of the excited atom. For clean metal surfaces with a high work function, deactivation takes place by an RI + AN mechanism. If the ionisation potential is smaller than the work function, the process takes place by an AD mechanism. It should be noted that the presence of an adsorbed layer, which changes the work function and the conditions on the metal surface, may lead to a change in the deactivation mechanism, and in a number of cases to the existence of both mechanisms.[95] An important feature is that, irrespective of the deactivation mechanism, the SEE efficiency is high. This makes it possible to use the magnitude of the emission of secondary electrons to estimate the intensity of the heterogeneous deactivation on metal surfaces. No systematic quantitative determinations of the coefficients of heterogeneous deactivation $\gamma$ for different metals have been carried out. Published data[95] indicate that on metals, the value of $\gamma$ is close to 1.

The study of the scattering of atoms and the ejection of electrons has recently been described. Thus the reflection of a beam of He* atoms from different surfaces has been studied by measuring the concentration of He($^1S$) atoms in

the gas phase.[121] The reflection coefficient of the He* atoms was $10^{-6}$ for Cu (110), $5 \times 10^{-6}$ for Pd (110), $1.5 \times 10^{-4}$ for polycrystalline W, $3 \times 10^{-3}$ for Pd covered with CO, and $5 \times 10^{-4}$ for oxidised Pd. Thus only a negligible fraction of the incident metastable He atoms are reflected from the surfaces of these metals, and the deactivation coefficient $\gamma$ is close to 1. In the same work it was found that the reflection coefficients of He*, Ne*, and Ar* atoms from the surface of single crystals of LiF and NaCl are also extremely low and are respectively $2 \times 10^{-4}$, $4.6 \times 10^{-2}$, and $2 \times 10^{-4}$ (LiF), and $1.2 \times 10^{-4}$, $2.8 \times 10^{-3}$, and $10^{-4}$ (NaCl), that is for the surfaces of these dielectrics, as in the case of metals, the deactivation coefficient is close to 1. The authors cited consider that these similar values of the reflection coefficients of the excited atoms for metals and dielectrics indicate that these quantities are independent of the nature of the surfaces. This conclusion, however, does not agree with the data obtained by other workers.

The reaction of beams of He atoms with the surface of the (110) face of a single crystal of tungsten was studied in Ref.122. It was established that the quantity of atoms reflected depends on the angle of incidence of the beam ($\theta$ is the angle between the direction of the beam and the normal to the surface). At low values of $\theta$, a small fraction of the atoms (less than 10%) is reflected, and the coefficient $\gamma > 0.9$. At high values of $\theta$ (70–80°), 50–60% of the incident metastable atoms are reflected, and $\gamma$ is 0.4–0.5. It was also found that for a clean surface, the yield of emitted electrons also depends markedly on the angle of incidence of the excited species, amounting to 5–8% at low angles of incidence and increasing markedly at high values of $\theta$ (60–80°). For an oxidised W surface, the yield reached 40%.

Comparison of published data[120–122] shows that: 1) the deactivation coefficient on metals may be lower than 1; 2) the yield of secondary electrons depends on the magnitude of the angle of incidence of the atoms and the presence of an adsorbed layer on the metal surface, so that the determination of the value of $\gamma$ from the emission of secondary electrons and the comparison of these values for different metals must be carried out with great care; and 3) the presence of an adsorbed layer on the metal surface leads to an increase in the yield of secondary electrons and the reflection coefficient of the metastable atoms.

It should be noted that in the works cited, the experiments were carried out with beams of atoms only on metal single crystals. It may be assumed that the coefficient $\gamma$ will not always be equal to 1 in the case of polycrystalline metal surfaces under flow or diffusion conditions.

There are very few published data for non-metal surfaces. The deactivation coefficients of metastable atoms on semiconductors and dielectrics have not bee measured, and there is no method for studying heterogeneous deactivation for non-metals which is an informative as the SEE method for metals.

Optical methods for recording metastable atoms (MA) in the gas phase, for example laser-induced fluorescence spectroscopy,[123] have not yet been used to study the heterogeneous deactivation of MA, and the traditional absorption-spectroscopic method for measuring rhe concentrations of these species in a flow system has been found to be unsuitable.[124,125] For these reasons, there are few published papers on the heterogeneous deactivation of MA on non-metal surfaces. Apart from the work examined,[121] there are only a few published studies. In Ref.124, the radial concentration gradient of MA of helium in the flux leaving a glow discharge was measured from the intensity of the luminescence (in the visible range) of different forms of helium MA. It was found that the He* atoms are not completely deactivated on the walls, and the deactivation coefficients on glass are 0.35 for He $2^1S$ and 0.11 for He $2^3S$. In Ref.125, an optical method was also used to determine the radial distribution of MA in a tube through which a stream of gas was passed after a discharge, and it was found that for Pyrex, $\gamma_{He^*} < 0.75$ and $0.12 < \gamma_{Ar^*} < 0.5$.

The reflection of a beam of inert gas MA from different surfaces has been studied.[126] The SEE was measured inside a metal cylinder when the MA struck the end face, which consisted of targets of different materials. The values of the reflection coefficients of the MA on glass and stainless steel were 0.01 for He*, 0.02 for Ne*, and 0.03 for Ar*, that is the values of $\gamma$ were close to 1. In Ref.155, the deactivation of excited argon ($^3P_2$) atoms in the gas phase was studied, and the deactivation coefficient on the walls of the quartz reactor estimated ($\gamma > 0.4$).

A new method was recently proposed[127,128,135] for measuring the coefficients of the heterogeneous deactivation $\gamma$ of metastable atoms, based on the use of semiconducting detectors of the active species.[129] A reversible change in the electrical conductivity of a film of ZnO activated by gold micro-crystals was detected on reaction with MAIG.[127] Comparison of the values of the initial rate of change in the electrical conductivity of the detector ($\nu$) and the emission current of the magnesium plate $I_m$ (the detector and the magnesium target were placed in the same vessel) under the conditions of the generation of MA of helium or krypton (a low-voltage discharge with an incandescent cathode, at $10^{-2}$ hPa and room temperature) showed that there is a linear relationship between $\nu$ and $I_m$. The emission current is proportional to the concentration of MAIG in the gas phase.[130] Thus a ZnO/Au film can be used as an MAIG proportional detector. In these experiments, the MAIG concentration was $10^7$–$10^8$ cm$^{-3}$. The range of concentrations measured can be extended considerably both into the range of lower MAIG concentrations (by increasing the sensitivity of the measuring scheme) and into the range of higher concentrations (by strobing the flux of MAIG reaching the ZnO/Au film).

This detector was used to determine the values of $\gamma$ on various surfaces.[127] The change in the concentration of MAIG was measured along a cylinder whose inner surface was covered with the substance being studied, with increase in the distance from the MAIG source. The coefficient $\gamma$ was calculated from the equation

$$\frac{2\gamma}{2-\gamma} = \frac{4Da}{c} \frac{I_1(ar)}{I_0(ar)}$$

where $D$ is the diffusion coefficient, $c$ the thermal velocity of the atoms, $r$ the radius of the vessel, $I_1$ and $I_0$ the Bessel functions of first and zeroth orders, $a$ the slope of the straight line ($n/n_0 - h$), $h$ the distance from the detector to the inlet into the cylinder, $n$ the MAIG concentration at a distance $h$, and $n_0$ the MAIG concentration at the inlet into the cylinder. To confirm that the constant obtained does in fact characterise the heterogeneous and not the homogeneous deactivation of the MA, the values of $\gamma$ in helium were determined at different pressures ($10^{-2}$–$10^{-3}$ hPa). It was found that in this range, $\gamma$ is independent of pressure, that is under the chosen conditions the homogeneous quenching of the excited atoms is not significant. The coefficients $\gamma$ on glass are $2.0 \times 10^{-3}$ (He*), $7.3 \times 10^{-3}$ (Kr*), $3.5 \times 10^{-3}$ (Xe*), and those on polycrystalline zinc oxide $3.4 \times 10^{-3}$, $4.1 \times 10^{-3}$, and $4.4 \times 10^{-3}$ respectively.

The authors cited[127] concluded that the method of detecting MA using semiconducting detectors is highly sensitive, produces little perturbation in the system being studied, and is most suitable for measuring $\gamma$ under diffusion conditions at low MA concentrations. The deactivation of inert gas MA on glass and ZnO is described by an equation of first order with respect to the MA concentration in the gas phase.

The same method was used to measure the values of $\gamma$ for discontinuous films of gold on glass and zinc oxide.[128] It was found that $\gamma$ depends on the gold concentration (the covering coefficient $f$) on the surface of the support. Thus for the Au/glass system, the value of $\gamma$ was 0.17 ($f$ = 0.13) or 0.37 ($f$ = 0.45), whereas for Au/ZnO the corresponding values of $\gamma$ were 0.11 and 0.38. The heterogeneous deactivation of the metastable atoms of inert gases on discontinuous films of gold apparently takes place on the surface of the metal particles, since the values of $\gamma$ and $f$ coincide. In this case the deactivation of the excited atoms takes place with an efficiency close to 1, whereas it is lower by a factor of 100 on the surface of the support, irrespective of the electronic structure of the carrier (dielectric, semiconductor).

Thus the results of the measurement of the coefficients of the heterogeneous deactivation of the metastable atoms of inert gases on non-metals are few and contradictory. For example, for glass the following values of $\gamma$ have been obtained: 0.35 and 0.11,[121] 0.75,[125] 1,[126] and $2 \times 10^{-3}$.[127] These marked differences are apparently related to the fact that in Refs.121, 125, and 126 the MA concentration was much higher than in Ref.127. In the deactivation of MA on non-metals, the excitation of the surface at sufficiently high concentrations of the excited species apparently facilitates the more effective loss of the energy of the excited atoms colliding with it.

Thus the deactivation of MA on non-metal surfaces takes place with a lower efficiency than on metal surfaces. In the last case the loss of the energy by the metastable atoms takes place chiefly in their reaction with the electronic system of the metal, leading to the emission of electrons. It is as yet difficult to say anything definite about the mechanism of the reaction of these species with non-metals.

The heterogeneous deactivation of electronically excited nitrogen molecules has been studied.[132,133] The longest-lived state was found to be $N_2(A^3\Sigma_u^+)$ with a radiative lifetime of 2 s. In Ref.133, the concentration of $N_2^*$ was measured from the photo-ionisation in a mass spectrometer, and also using a platinum calorimeter with a stream of nitrogen passed through a discharge ($p$ = 0.6–7 hPa). The coefficient of heterogeneous deactivation was found to be $3 \times 10^{-5}$, that is the efficiency of the deactivation of $N_2^*$ on the glass walls is very low. The dependence of the value of $\gamma$ on the concentration of excited nitrogen molecules was established;[132] the coefficient $\gamma$ is low ($7 \times 10^{-4}$) at low concentrations, and high (0.5) at high concentrations. Thus the concentration dependence of $\gamma$ obtained for metastable nitrogen molecules was the same as that for metastable inert gases on a glass surface.

There are practically no published data on the deactivation of excited metal atoms on solid surfaces. Only a few papers have dealt with the reaction of excited mercury atoms with semiconducting films of zinc oxide.[136–138] The change in the electrical conductivity ($\sigma$) of ZnO films under the influence of mercury atoms (Hg*), obtained by photo-excitation in the gas phase (non-excited Hg atoms have no influence on $\sigma$), was studied. At room temperature the reaction with Hg* atoms produces a marked increase in $\sigma$ for the ZnO films, and at "saturation" of the signal, $\sigma$ increases by 80%. The authors cited attributed the effect of "saturation" of the change in $\sigma$ to two processes taking place simultaneously on the ZnO surface: 1) the formation on the surface of zinc atoms, which bring about an increase in $\sigma$ for ZnO:[114]

$$ZnO + Hg^* \rightarrow (HgO)_s + Zn_s \qquad (6)$$

(s = surface); and 2) the formation of surface zinc mercurides, which, like metal molecules (for example $Ag_2$),[114] apparently have no influence on the electrical conductivity of semiconducting films

$$Zn_s + Hg^* \rightarrow (HgZn)_s \qquad (7)$$

The simultaneous processes (6) and (7) are responsible for the establishment of the stationary value of $\sigma$ for ZnO on bombardment of its surface.

The proposed scheme was verified by experiments in which zinc atoms were deposited on the ZnO surface, or oxygen was adsorbed on it. On the films activated by zinc atoms, the magnitude and the sign of the change in $\sigma$ depend on the concentration of Zn atoms; at high zinc concentrations, the value of $\sigma$ for ZnO decreases under the influence of Hg* atoms (process 7). On ZnO films treated with oxygen, the magnitude of the change in $\sigma$ for ZnO increases (process 6).

In Refs.136–138 it was established that at a definite concentration of previously deposited zinc atoms, the value of $\sigma$ for ZnO remains unchanged under the influence of Hg* atoms. From the change in the electrical conductivity of the adsorbate, the authors cited reached conclusions about the dissociation of the molecules adsorbed on ZnO in their reaction with excited mercury atoms. A marked increase in $\sigma$ took place after the adsorption of hydrogen on bombardment with Hg* atoms, indicating that $H_2$ is dissociated to atoms, since it was previously shown[114] that H atoms are electron donors on a ZnO surface. The same effect was detected for adsorbed isopropyl alcohol.

Thus the action of excited mercury atoms (and possibly other metal atoms) leads to a change in the chemical composition of the clean surface of oxide semiconductors, and also of the adsorbed layer.

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# Zirconium Complexes in Synthesis and Catalysis

U.M.Dzhemilev, O.S.Vostrikova, and A.G.Ibragimov

Data on the use of organometallic complexes of zirconium as key intermediates in organic synthesis and the catalysis of the transformations of alkenes, dienes, and acetylenes have been systematised. The hydrozirconation of unsaturated compounds and the reactions of alkyl- and alkenylzirconium complexes with electrophilic reagents, $\alpha,\beta$-unsaturated ketones, aryl and vinyl halides, and salts of transition and non-transition metals have been examined. The use of zirconium complexes as catalysts in the homogeneous hydrogenation, isomerisation, linear dimerisation, and oligomerisation of alkenes and dienes, and the hydro- and carbometallation of the latter, have been considered. The mechanisms of these reactions have been discussed. The bibliography contains 147 references.

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## I. INTRODUCTION

Many of the most important achievements in organic chemistry in the last 15–20 years have been associated in some way with the use of transition metal complexes. Among these complexes, an increasingly important place is occupied by zirconium compounds, which have a number of unique properties enabling them to be used as highly reactive reagents in organic synthesis, and also as effective catalysts for transformations of unsaturated hydrocarbons and organometallic compounds. The discovery of the reaction of organozirconium intermediates with transition metal complexes, involving the transfer of alkyl or alkenyl substituents from the zirconium atom to other metals, has made it possible to carry out the stereoselective synthesis of compounds with a definite structure, whose preparation by other methods is extremely complicated.

Extensive material on the use of zirconium complexes in synthesis and catalysis has now accumulated, and studies in this field are being carried out actively in the Soviet Union and abroad. Although some aspects of the use of zirconium derivatives in organic synthesis have been discussed in two reviews,[1,2] there is a large amount of material which did not appear in these reviews. A large amount of data on the use of zirconium compounds as homogeneous metal-complex catalysts (published mainly in the last five years) has not yet been discussed and systematised.

The present review gives the most important results of studies of the use of organozirconium compounds in organic synthesis and metal-complex catalysis, published chiefly in the last ten years. The polymerisation of unsaturated compounds on zirconium-containing catalysts is not examined.

## II. THE SYNTHESIS AND TRANSFORMATIONS OF ALKYL- AND ALKENYLZIRCONIUM COMPLEXES

### 1. The Hydrozirconation of Unsaturated Compounds

About ten years ago it was established[3,4] that bis(cyclopentadienyl)zirconium chloride hydride $Cp_2Zr(Cl)H$ (I) and bis(cyclopentadienyl)zirconium dihydride $Cp_2ZrH_2$ react readily with alkenes or acetylenes to give fairly stable alkyl and alkenyl complexes of zirconium. Subsequently, Schwartz and co-workers[1] developed a number of promising schemes for the use of hydrozirconation products as active intermediates in organic synthesis. In the last ten years, hydrozirconation has become popular in organic synthesis, chiefly as a result of these studies, as indicated by the fact that the hydride complex (I) is often referred to in the chemical literature as the "Schwartz reagent".[5]

The hydrozirconation of linear and cyclic alkenes by bis(cyclopentadienyl)zirconium chloride hydride (I) takes place under mild conditions and with high yields, giving alkyl complexes $Cp_2Zr(Cl)R$. The latter, unlike their lower homologues, are fairly stable.[6] The hydrozirconation of alkenes using $Cp_2Zr(Cl)H$ or $Cp_2ZrH_2$ takes place strictly as a 1,2-addition and is highly regioselective, reacting with both mono- and disubstituted alkenes to give only the primary alkylzirconium complexes, which are readily split by electrophiles (Table 1).

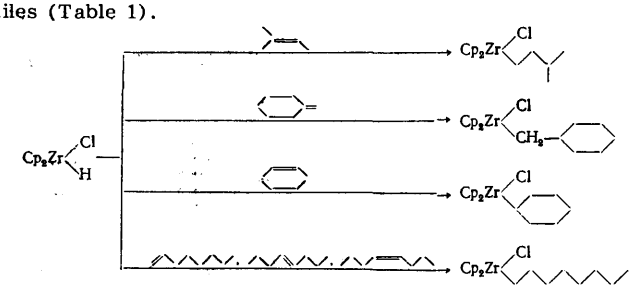


**Table 1.** Hydrozirconation of alkenes using compound (I).[6]

| Alkene | Electrophilic reagent | Reaction product | Yield, %* |
|---|---|---|---|
| Oct-1-ene or oct-4-ene | HCl (dil.)** | octane | 100 |
| Ditto | $Br_2$ | 1-bromo-octane | 96 |
| » | $I_2$ | 1-iodo-octane | 91 |
| » | $PhICl_2$ | 1-chloro-octane | 65 |
| » | $MeC(O)Cl$ | decan-2-one | 80 |
| 2-Methylbut-1-ene | $Br_2$ | 1-bromo-3-methylbutane | 100 |
| » | $MeC(O)Cl$ | 5-methylhexan-2-ol | 72 |
| Cyclohexene | $Br_2$ | bromocyclohexane | 95 |

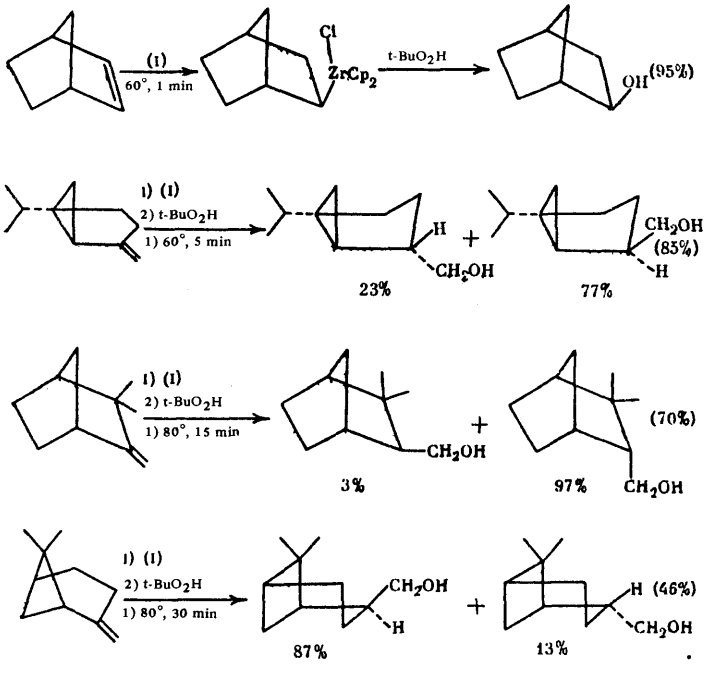
*Calculated for $Cp_2ZrCl_2$.
**Temperature 0°.

It is noteworthy that the hydride complexes of zirconium give exclusively primary alkylzirconium organic metallic compounds, irrespective of the position of the double bond

in the original alkene. Under hydrozirconation conditions, repeated addition and elimination of hydride complexes of zirconium probably take place, giving finally the thermodynamically most stable primary alkylzirconium complexes. These transformations take place fairly rapidly and under mild conditions, unlike the corresponding reactions of organoboron and organoaluminium compounds.[7,8] For example, the hydrozirconation of symmetrical disubstituted alkenes containing 24–42 carbon atoms gives only primary alkylzirconium complexes.[9] To obtain the optimum yields (50–80%) of the desired products in these experiments, however, the reaction must be carried out for 1–6 d at 40°.

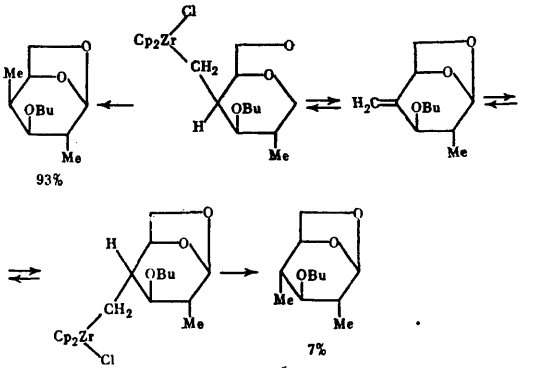
According to Schwartz's data, the relative rate of the hydrozirconation of alkenes decreases in the order: α-alkene > *cis*-alkene > *trans*-alkene > exocyclic alkene > cyclic alkene > trisubstituted alkene; the last three alkenes react with $Cp_2Zr(Cl)H$ at temperatures not lower than 40°.[1,6] Bulky groups in the substituted alkenes probably create steric hindrance to the approach of the zirconium hydrides, which have a "sandwich" structure, to the reaction centre. Thus tetrasubstituted alkenes and also methylcyclohexene and cyclo-octene do not react with $Cp_2Zr(Cl)H$ even when kept at 40° for a long time.[6]

In a series of bicyclic hydrocarbons with double bonds shielded to different extents, the rate of hydrozirconation decreases sharply in the order: norbornene > sabinene > camphene > β-pinene,[10] and the addition of the hydride complex (I) takes place chiefly on the least shielded side. The highest stereoselectivity of the addition is observed for camphene.

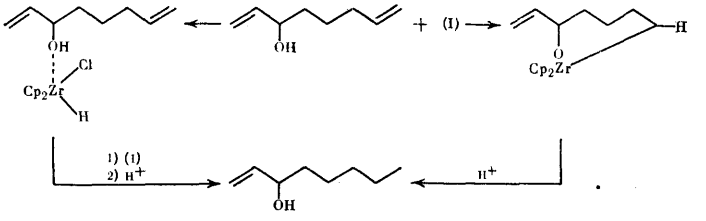



The anomalously high yield of 10-isothujanol in the oxidation of the hydrozirconation products of sabinene was attributed[10] to electronic factors.

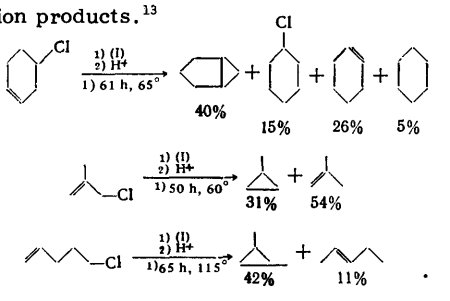
Hydrozirconation with subsequent protolysis made it possible to carry out the stereoregulated reduction of a methylene derivative of a monosaccharide in the synthesis of the C(9)–C(19) fragments of the antibiotics oleandonolide and erythronolide B.[11]



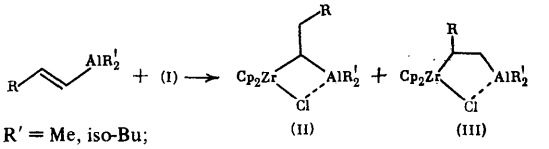

In this case the predominant formation of the thermodynamically more favourable galacto-isomer indicates that kinetic factors have a decisive influence. The hydrozirconation of unsaturated compounds is not only highly regiospecific but also highly selective. In particular, the hydrozirconation of non-conjugated dienols takes place exclusively at the double bond farthest from the hydroxyl group.[12] The high selectivity of this reaction is evidently due to the formation of a complex of the dienol with the hydride (I), which then reacts with a second $Cp_2Zr(Cl)H$ molecule at the sterically least hindered C(7)–C(8) vinyl group. It is not excluded that in these experiments, intramolecular hydrozirconation involves the formation of an alkoxyzirconium hydride according to the scheme:




In the reaction of $Cp_2Zr(Cl)H$ with various γ-halogenoalkenes, cyclopropane derivatives are formed in addition to the dehalogenation products.[13]

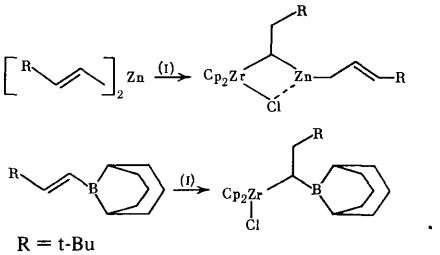



Complex (I) can hydrozirconate not only the simplest alkenes and dienes but also unsaturated organoaluminium, -zinc, and -boron compounds.[14] The hydrozirconation of alkenyldialkylalanes by $Cp_2Zr(Cl)H$ gives a bimetallic complex containing a bridging chloride ligand. The regioselectivity of the addition of the hydride (I) to the double bond depends on the size of the alkyl substituents on it.



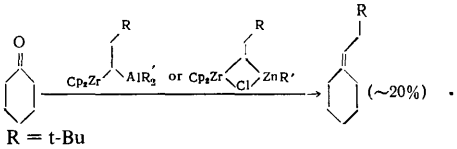

R′ = Me, iso-Bu;
R = t-Bu, (II) : (III) = >20 : 1
R = n-Bu, (II) : (III) = 3 : 2
R = Me, (II) : (III) = 1 : 2 .

Dineohexenylzinc forms with $Cp_2Zr(Cl)H$ an analogous bimetallic cyclic complex, whereas the neohexenyl derivative of borane reacts with compound (I) according to the usual scheme.[14]



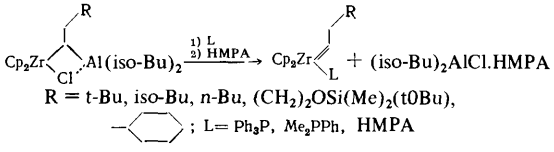
R = t-Bu

The zirconium complexes obtained are of interest as analogues of "Wittig's reagent" in carbonylalkenylation.[14]



R = t-Bu

More active analogues of "Wittig's reagent" are the carbene complexes of zirconium formed by the reaction of the above zirconium–aluminium complexes with a mixture of hexamethylphosphamide (HMPA) and a stabilising ligand (for example $PhP_3$, $Me_2PPh$, or an excess of HMPA).[15]



R = t-Bu, iso-Bu, *n*-Bu, $(CH_2)_2OSi(Me)_2(t0Bu)$, ; L= $Ph_3P$, $Me_2PPh$, HMPA

The reagents obtained convert esters and ketones into the corresponding alkenes in 78–100% yield.

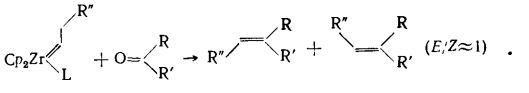
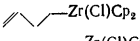
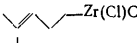
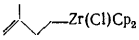
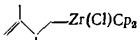
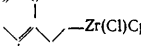
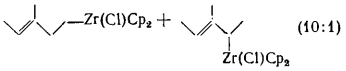
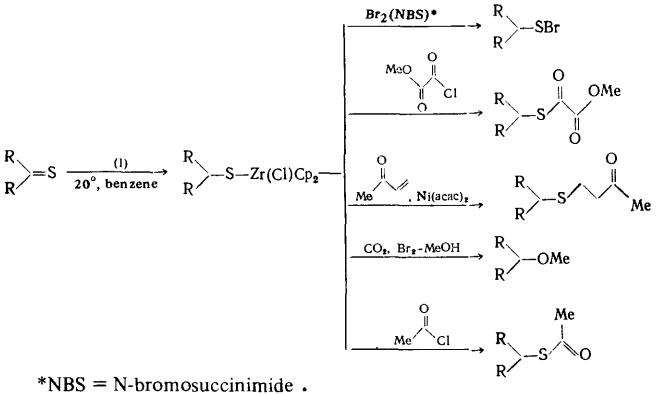


Table 2. Hydrozirconation of 1,3-dienes using compound (I).[1,18]

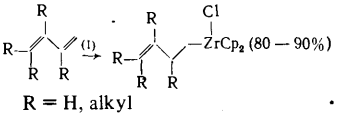
| 1,3-Diene | Product |
|---|---|
|  |  |
|  |  |
|  |  |
|  |  |
|  |  |
|  |  (10:1) |

An attempt has been made to hydrozirconate heteroalkenes, in particular Schiff bases, in order to subsequently transform them into amides.[16] It was found, however, that complex (I) does not add on to a C=N bond but transforms Schiff bases into enamides and imides, apparently via a Zr–enamide complex. At the same time, aromatic and aliphatic thioketones, including the α, β-unsaturated compounds, are smoothly hydrozirconated by $Cp_2Zr(Cl)H$ at room temperature to give compounds with a Zr–S bond, which can readily be converted into various sulphur-containing compounds under very mild conditions.[17]



*NBS = N-bromosuccinimide .

Unlike monoalkenes, 1,3-dienes undergo hydrozirconation much more slowly (by a factor of ~50) to give γ,δ-unsaturated zirconium complexes.[18] The reaction takes place mainly by the 1,2-addition of complex (I) at the sterically least hindered double bond of the diene (Table 2).



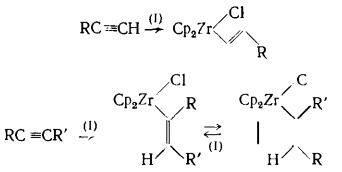
R = H, alkyl

Thus "Schwartz's reagent" as a hydrometallating agent is superior not only to the hydrides of boron and aluminium, which in the case of 1,3-dienes give a complex mixture of products,[19,20] but also to the hydrides of most transition metals, which react with conjugated dienes to form both 1,2- and 1,4-addition products.[21]

A review by Schwartz[1] contains the only mention of the possibility of carrying out the reaction between 2,4-dienes and three equivalents of $Cp_2Zr(Cl)H$, but no data on the structure of the products are given. There are no published data on the hydrozirconation of allenes.

The protonation of Vitamin $D_3$ and its 5*E*-isomer illustrates the possibility of hydrozirconating conjugated trienes.[22] The activity of the hydride complex (I) in this reaction is greater than that of 9-borabicyclononane. Irrespective of the structure of the original trienes, hydrolysis gave a mixture of the 5*E*- and 5*Z*-dihydrovitamins, indicating that the reaction is accompanied by 5*Z* ⇄ 5*E* isomerisation. Thus the sterically more hindered 5*Z*-isomer is hydrozirconated much more slowly. This reaction is apparently the only example of the hydrozirconation of 1,3-dienes containing functional substituents.[22]

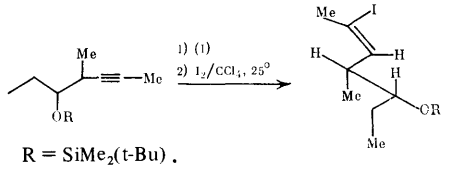
The addition of $Cp_2Zr(Cl)H$ to acetylenes is ~70–100 times more rapid than that to alkenes with analogous structures. Monosubstituted acetylenes form exclusively the 1*E*-alkenylzirconium complexes, and the disubstituted compounds give a mixture of the two possible isomers, the ratio of which depends on the structure of the alkyl substituents;[23,24] 1-alkenylzirconium complexes, unlike their alkyl analogues, do not undergo the above isomerisation, which takes place with the migration of the zirconium atom to the end of the carbon chain.



R = H, Me; R′ = Et, n-Pr, iso-Pr, n-Bu, iso-Bu, t-Bu.

In a number of cases, in the hydrozirconation of unsymmetrical disubstituted acetylenes with bulky substituents, the addition of complex (I) is highly regioselective.

Thus the hydrozirconation of 4-methyl-5-(dimethyl-t-butylsiloxy)-hept-2-one with one equivalent of compound (I) gave a single alkenylzirconium complex, which was readily converted into the corresponding halogenoalkene by treatment with $I_2$.[25]



R = $SiMe_2$(t-Bu).

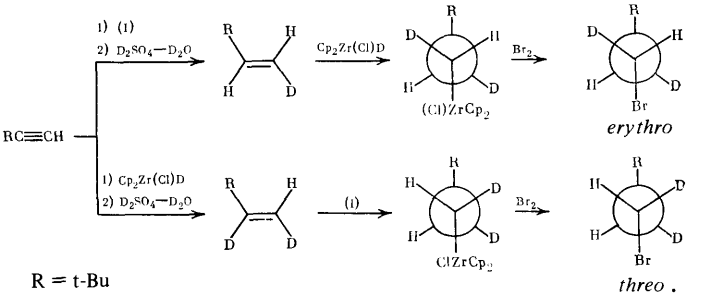
It should be noted that in the hydrozirconation of acetylenes with an excess of compound (I), stereo- and regioselective isomerisation of the resulting alkenyl complexes of zirconium is observed, giving organometallic compounds in which the zirconium atoms are situated predominantly on the least shielded side.[1,23]

Published data on the hydrozirconation of acetylenes indicate that $Cp_2Zr(Cl)H$ is currently one of the most active and regioselective reagents, capable of hydrometallating acetylenes, including those containing such functional substituents as Cl, OH, OR, $CO_2H$, C≡N, $CO_2R$, and in the case of the last two groups no appreciable reduction is observed in the reaction.[26] Thus $Cp_2Zr(Cl)H$ acts as a universal, highly active, and selective hydrometallating agent for a wide range of unsaturated compounds.

It has recently been shown possible to use $Cp_2Zr(Cl)H$ and its derivatives as reducing agents. Thus for example "Schwartz's reagent" (I) reduces cyclic ketones stereoselectively to the corresponding axial alcohols.[27] The mixed zirconium hydride $Cp_2Zr(Cl)BH_4$ has been proposed[28] for the selective reduction of aldehydes and ketones in the presence of carboxylic acids, esters, nitriles, and nitroalkanes. This reducing agent is more selective than the known derivatives $LiAlH_4$, boranes, and trialkyl borohydrides, and does not require the use of an inert atmosphere.

## 2. Reactions of Alkyl- and Alkenylzirconium Complexes with Electrophilic Reagents

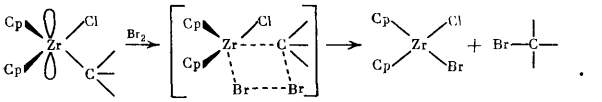
Alkyl- and more particularly alkenylzirconium complexes are convenient intermediates in the functionalisation of unsaturated compounds. One of the simplest ways of functionalising these compounds is by the stereospecific splitting of Zr–C bonds by electrophilic reagents. This process has been studied in considerable detail for a wide range of electrophilic reagents. Alkyl or alkenyl halides are readily formed by the reaction of the corresponding alkyl- and alkenylzirconium complexes with halogens and *N*-halogenosuccinimides. For the example of the reaction of bromine with the *erythro*- and *threo*-forms of the complex $Cp_2Zr(Cl)CHD–CHD–CMe_3$ it was shown that the formation of the alkyl halide molecules takes place with preservation of the configuration of the substituents on the carbon atom joined to Zr, indicating that the reaction involves a cyclic intermediate state.[2,29]



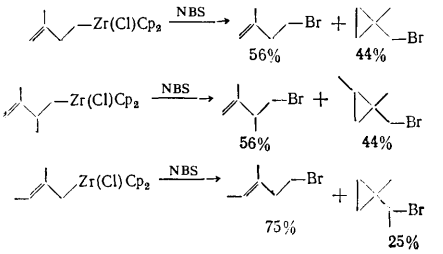
R = t-Bu

*threo*.

According to the proposed mechanism, the electrophilic reagent reacts with the substrate to form a cyclic intermediate complex using an unoccupied low-lying orbital of zirconium; this facilitates frontal attack at the Zr–C bond, and the subsequent polarisation of the coordinated electrophilic reagent leads to the rupture of this bond.



Similar reactions with $Br_2$ and N-bromosuccinimide (NBS) are undergone by alkyl- and alkenylzirconium complexes, the latter with preservation of the geometry of the double bond.[18,29] An exception is provided by 3-alkenylzirconium complexes containing, in addition to the double bond, alkenyl substituents on the C(3) atom. Under the influence of NBS, they are partly converted into cyclopropylalkyl bromides.[18]

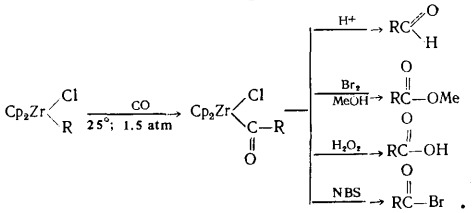


According to Schwartz's data,[29,30] alkylzirconium complexes are oxidised at the Zr–C bond in satisfactory yields by $O_2$, $H_2O_2$, alkyl hydroperoxides, and peroxyacids. In the later paper,[31] however, it was noted that in the oxidation of $C_8$–$C_{30}$ alkylzirconium complexes, reproducible high (~70%) yields of primary alcohols can be obtained only using anhydrous t-butyl hydroperoxide. The use of a 70% solution of the hydroperoxide in water gives mainly hydrocarbons, and the yields of alcohols are low, and decrease with increase in the length of the hydrocarbon chain. The formation of appreciable quantities of unsaturated hydrocarbons was also observed in the oxidation of the products of the hydrozirconation of β-pinene and camphene by a 95% aqueous solution of t-butyl hydroperoxide.[10]

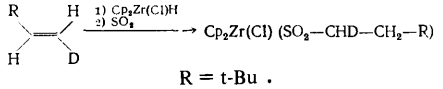
The presence, in the hydrocarbon group of the alkyl peroxide complexes, of double bonds separated by several carbon atoms from the metal atom has practically no influence on the oxidation, whereas the 1*E*-alkenylzirconium complexes cannot be oxidised smoothly.[1]

A convenient method for functionalising unsaturated compounds via the preparation of alkyl- and alkenylzirconium complexes is by the reaction of the latter with CO.[18,32] It is suggested that this reaction involves the rapid and reversible coordination of CO to the central metal atom to give a coordinatively unsaturated carbonyl complex $Cp_2Zr(Cl)(R)-CO$, in which the alkyl substituent migrates slowly to the active CO ligand.[2,32]

The relative ratio of formation of acyl complexes of zirconium depends markedly on the nature and structure of the alkyl substituent.[1] The acyl complexes can readily be selectively converted into aldehydes, carboxylic acids, esters, or acid halides, according to the scheme:



The analogous reaction of alkyl complexes of zirconium with $CO_2$ and $SO_3$ has not yet been carried out. Coordinatively saturated O,O'-sulphinate complexes of zirconium have been obtained using $SO_2$.[29]

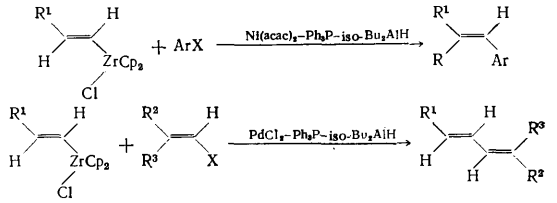


R = t-Bu .

In an excess of $SO_2$, this reaction is more complex.[33] $Cp_2Zr.(Cl)CH_3$ reacts similarly with $NO_2$ to give a zirconium complex of methylnitrosohydroxylamine.[34]

### 3. Alkenylzirconium Complexes in Cross-Coupling Reactions with Aryl and Vinyl Halides

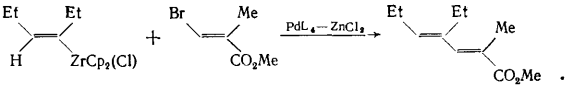
Negishi and co-workers were the first to establish that 1*E*-alkenylzirconium complexes in the presence of catalytic quantities of nickel or palladium compounds react readily with aryl[35] and vinyl[35-37] halides to give respectively derivatives of the arylethylene or dienes in 97–98% yield. The reaction is highly stereospecific (not less than 97%).



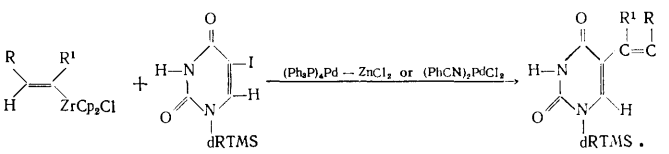
X = Cl, Br, I .

Attempts to extend the range of application of this reaction encountered serious difficulties. In particular, the formation of molecules of cross-coupled dienes, which takes place without complications in the case of β-monosubstituted alkenyl derivatives of zirconium, is extremely non-selective and gives low yields when the alkenyl substituents in the zirconium compounds are α, β- and β,β'-disubstituted. These difficulties were overcome by increasing the activity of the catalyst using promoting additives. The additives were salts of metals with electronegativities comparable with that of Zr, Ni, or Pd, but a much smaller atomic radius (Cu, Zn, Cd, Sn, In, Ti). Zn and Co salts were found to be most effective.

For example, the reaction between a 1*E*-alkenyl complex of zirconium and methyl β-bromomethacrylate in the presence of 5% $Pd(Ph_3P)_4$ after 6 h gives an ester of 2-methyl-4-ethyl-2*E*, 4*E*-heptadienoic acid in 22% yield, whereas with the "tandem" $(Ph_3P)_4Pd-ZnCl_2$ (1:1) the required product is formed in ~80% yield in 1 h.[38,39]

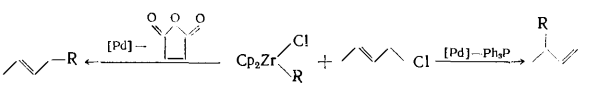


The same catalyst was used in the synthesis of 5*E*-alkenyl-substituted 2-deoxyuridines by cross-coupling 5-iodo-O-3',5'-bis(trimethylsilyl)deoxyuridine with α-substituted alkenylzirconium complexes obtained from disubstituted acetylenes. In the case of less hindered alkenylzirconium complexes, the most active cross-coupling catalyst was found to be the complex $(PhCN)_2PdCl_2$.[26]



where dTRMS represents O-3',5'-bis(trimethylsilyl)deoxyribose.

The influence of the nature of the ligands on the regioselectivity of the reaction has been demonstrated for the example of the cross-coupling of alkenylzirconium complexes with allyl halides and allyl acetates in the presence of bis-π-crotylpalladium chloride.[40] The introduction of phosphine ligands into the palladium catalyst promotes the coupling of the allyl fragment at the sterically more hindered end, whereas the addition of maleic anhydride favours the formation of the coupling products with the other structure.

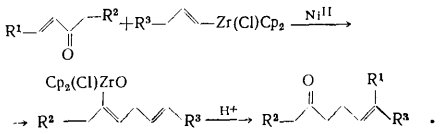


[Pd] = bis-π-allylpalladium chloride .

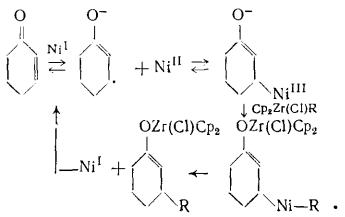
A similar influence of the ligands is observed in the coupling of alkenylzirconium compounds with stoichiometric quantities of π-allylpalladium chloride complexes. This made it possible to carry out an elegant regioselective synthesis of 20(S)-cholestan-3-one and 20(R)-cholestan-3-one.[41,42]

### 4. The Reactions of Alkenylzirconium Complexes with α,β-Unsaturated Ketones and the Transformations of Zirconium O-Enolates

Individual alkenyl complexes of zirconium react with α,β-unsaturated ketones even in the absence of catalysts, but the reaction is very slow, and the yields of required products are low.[43] Attempts to catalyse this reaction by transition metal complexes have been unsuccessful, probably because of the low activity of alkylzirconium complexes in *trans*-metallation. At the same time, the addition of 1*E*-alkenylzirconium complexes to enones is successfully catalysed by Ni compounds.[44,45] The corresponding β-alkenyl-substituted ketones are formed in high yield.

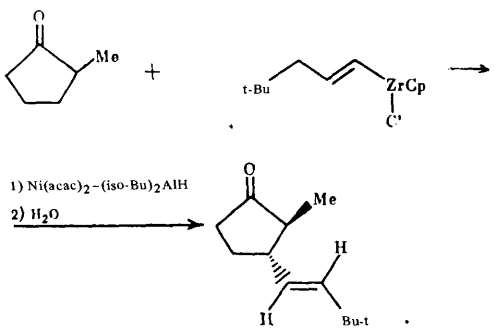


The catalytic systems obtained by reducing Ni compounds with $(iso\text{-}Bu)_2AlH$ are more active catalysts than nickel(II) salts. Moreover, an electrochemical study of the reaction of alkenylzirconium complexes with α,β-unsaturated ketones showed that this reaction, like the cross-coupling of vinyl complexes of zirconium with aryl and vinyl halides, is catalysed by nickel(I) complexes. On the basis of the results obtained, the following mechanism was proposed for the alkylation of enones.[46,47]

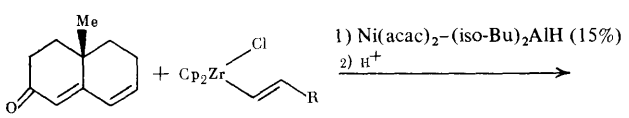


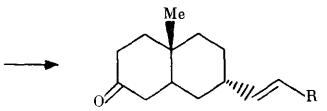
According to this scheme, the first stage involves the transfer of an electron from $Ni^I$ to the enone, followed by the oxidative addition of the ketyl to $Ni^{II}$, giving a σ-bonded complex of $Ni^{III}$ with the enone. The subsequent transformations of this complex as a result of *trans*-metallation and reductive elimination give the Zr enolate with the simultaneous regeneration of $Ni^I$.

The yield of the products of the 1,4-addition of 1*E*-alkenylzirconium complexes to enones is influenced considerably by the structure of the original ketone. The reaction gives good yields with most cyclic and acyclic ketones (Table 3), but in the case of $\Delta^{1(9)}$-octen-2-one and 10-methyl-$\Delta^{1(9)}$-octenone the yields of the products of the coupled addition do not exceed 33% and 70% respectively. Like the cuprate method, the addition of alkenylzirconium complexes to α-substituted cyclic enones gives the *trans*-disubstituted ketones with the same stereochemistry.[45]

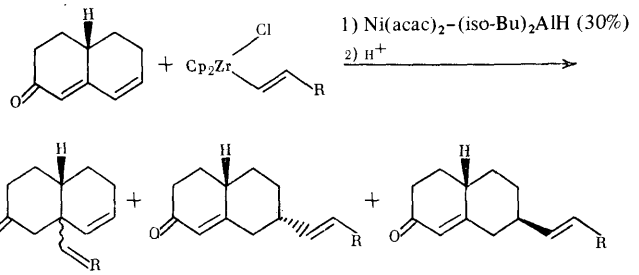


The selectivity of the alkylation of dienones depends to a marked extent on their structure. For example, the addition of alkenylzirconium complexes to 10-methyl-1(9),7-hexalin-2-one takes place selectively to give a single isomer, whereas in the case of non-substituted 1(9),7-hexalin-2-one, a mixture of regio- and stereoisomers is obtained.[47]





62% (R = n-Bu)
77% (R = t-Bu)

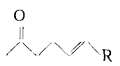
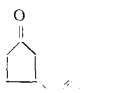
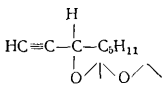
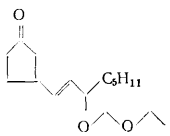
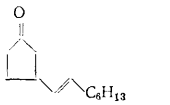
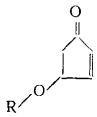
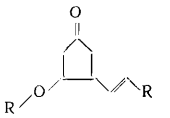
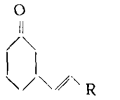
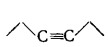
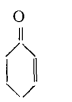
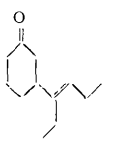
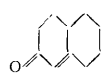
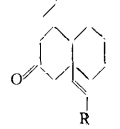
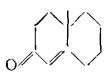
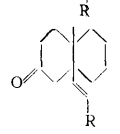


3% (R = n-Bu)
8% (R = t-Bu)

27% (R = n-Bu)
13% (R = t-Bu)

19% (R = n-Bu)
15% (R = t-Bu) .

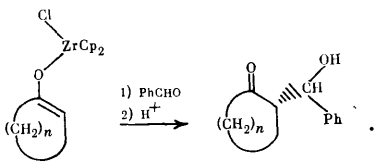
Table 3. Addition of alkenylzirconium complexes to α,β-enones, catalysed by nickel salts*.[44,45]

| Acetylene | α,β-Enone | Product | Yield, % |
|---|---|---|---|
| HC≡C—R |  |  | >35 |
| HC≡C—R |  |  | 78 |
|  |  |  | 59 |
| HC≡CC$_6$H$_{13}$ |  |  | 49 |
| HC≡C—R |  |  | 76,9 |
| HC≡C—R |  |  | 77 |
|  |  |  | 6—10 |
| HC≡C—R |  |  | 32,2 |
| HC≡C—R |  |  | <10 |

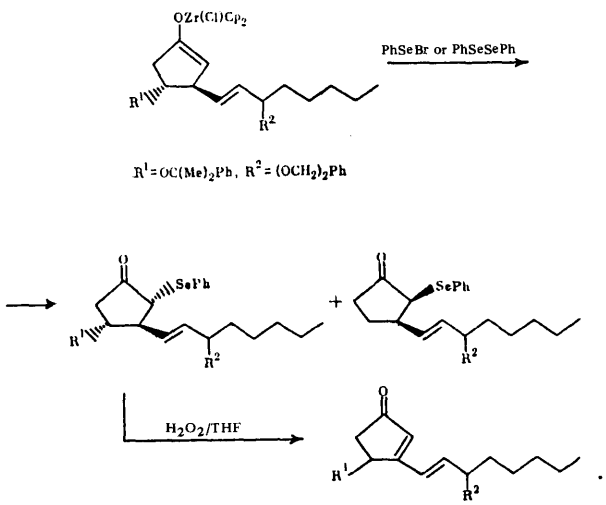
*R = t-Bu.

The highly reactive zirconium enolates formed have been made the basis of promising methods for obtaining β-keto- and homoallyl alochols of definite structure, used as synthones in the synthesis of natural compounds. Thus hydrozirconation and the coupled addition of alkenylzirconium complexes to cyclopentenone derivatives have been used to synthesise analogues of prostaglandins.[45,48]

Attempts to use alkyl and allyl halides to introduce a substituent into the α-position of β-substituted Zr enolates were unsuccessful, but Zr cyclopentenolate reacts readily with a solution of monomeric formaldehyde in ether, to give after hydrolysis α-hydroxymethylcyclopentenone in 70% yield. When formaldehyde is replaced by acetaldehyde, the yield of desired products decreases sharply,[48] evidently as a result of steric hindrance, since non-substituted Zr O-cycloalkenolates react readily with benzaldehyde.[49]

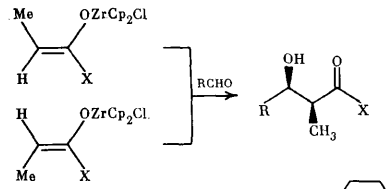


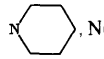

The reaction of zirconium O-enolates with selenium derivatives (PhSeBr, Ph–Se–Se–Ph) gives α-phenylselenylcyclopentanones, used as synthones in the preparation of analogues of prostaglandins.[50]



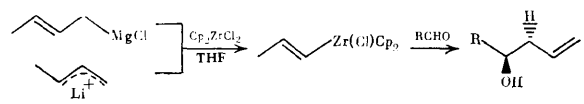

The use of zirconium O-enolates opens up an original approach to diastereoselective aldol condensation, which is generally carried out using prochirally pure enolates or enolates enriched in one of the isomers, which are difficult to obtain. Thus *Z*-enolates usually react with carbonyl compounds to give *erythro*-adducts, and *E*-enolates give *threo*-adducts. Since in the enolates of cyclic ketones the double bond has a fixed *E*-geometry, the preparation of *erythro*-aldols from these materials is complicated.

In 1980, almost simultaneously, two groups of workers reported that zirconium O-enolates, irrespective of their geometry and the nature of the substituents, react with aldehydes to give β-hydroxyketones, esters, and amides, with predominantly the ***erythro***-configuration.[49,51,52]




X = SBu-t, OMe, Ph, Et, OBu-t,  , N(iso-Pr)$_2$;
R = Ph, n-Pr, iso-Pr, C(CH$_3$) = CH$_2$ .

An interesting feature is that crotyl derivatives of zirconium, which can readily be obtained from crotylmagnesium chloride or crotyl-lithium and $Cp_2ZrCl_2$ in THF, react with aromatic and aliphatic aldehydes to give high yields of β-methylhomoallyl alcohols with predominantly the *threo*-configuration (yield 85–95%, selectivity 73–94%).[54]




## 5. Reactions of Alkyl- and Alkenylzirconium Complexes with Salts of Transition and Non-transition Metals

Considerable progress in the chemistry of organozirconium compounds was made with the discovery of the reaction involving the stereospecific transfer of a σ-bonded organic ligand from a zirconium atom to a metal atom which together with its ligand environment is more electronegative than the species $Cp_2Zr(Cl)^-$. The use of this reaction made it possible to overcome the difficulty of the low reactivity of alkyl- and alkenylzirconium complexes towards alkylating electrophilic reagents.

The first example of the use of these reagents to form a carbon–carbon bond was the reaction of alkyl- and alkenylzirconium complexes with $AlCl_3$, discovered in 1976.[54]

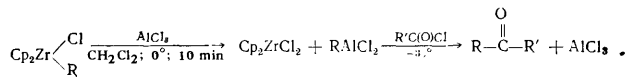


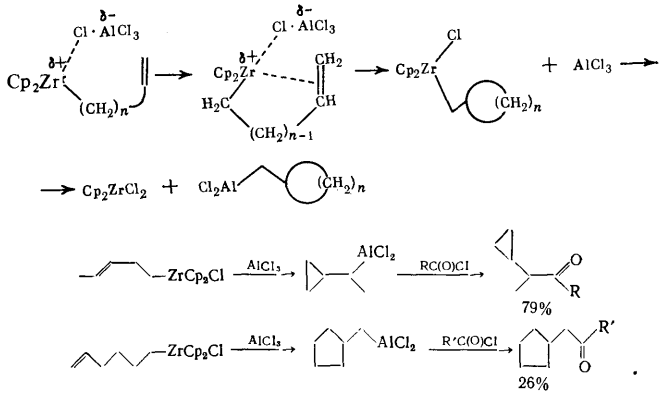

Table 4. Hydroalumination of cyclo-alkenes using (iso-Bu)$_2$.AlH (alkene : Al : $ZrCl_4$ : n-BuOH = 50 : 50 : 1 : 4; hexane).[107]

| Alkene | Yield*, % | T, °C | *t*, h |
|---|---|---|---|
| Cyclopentene | 100 | 20 | 6 |
| Cyclohexene | 99.5 | 20 | 8 |
| Cyclohexene | 100 | 40 | 2 |
| Cycloheptene | 82.6 | 20 | 24 |
| Cyclo-octene | 20 | 20 | 24 |
| Cyclo-octene | 20 | 60 | 12 |
| Cyclododecene (*cis* + *trans*) | 59.2 | 20 | 21 |
| Norbornene | 100 | 0 | 1 |
| Methylcyclobut-1-ene | 0 | 20 | 24 |
| Methylcyclododec-1-ene | 0 | 20 | 24 |

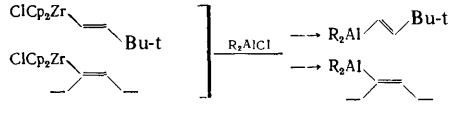
*Calculated for the cycloalkane.

The alkyl- or alkenylaluminium chlorides formed were used as acylating agents to obtain ketones, including enones, which cannot be synthesised by the direct acylation of the corresponding alkenyl-zirconium complexes (Table 4).

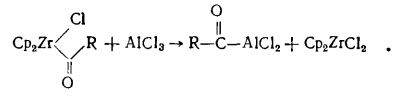
As a rule, the configuration of the double bonds of the alkenyl complexes remains unchanged in *trans*-metallation and subsequent transformations. In a number of cases, however, the reaction with ω-alkenylzirconium complexes is more complicated, and is accompanied by intramolecular cyclisation. This method was used to obtain a number of ketones which are difficult to prepare.[43]



According to Ref. 43, the reaction of alkylzirconium complexes with $AlCl_3$ is much slower than that of the corresponding alkenyl derivatives. Moreover, alkyl complexes of zirconium react with an excess of $AlCl_3$ to form exclusively monoalkylaluminium chlorides, whereas the alkenyl complexes may give mono-, di-, and trialkenylalanes, depending on the Zr:Al ratio. This method has been used to obtain mixed dialkenylalanes with different structures.

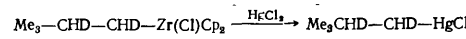


Acyl complexes of Zr react similarly with $AlCl_3$ to give acyldihalogenoalanes, which are of interest as potential equivalents of the acyl anion.[55]

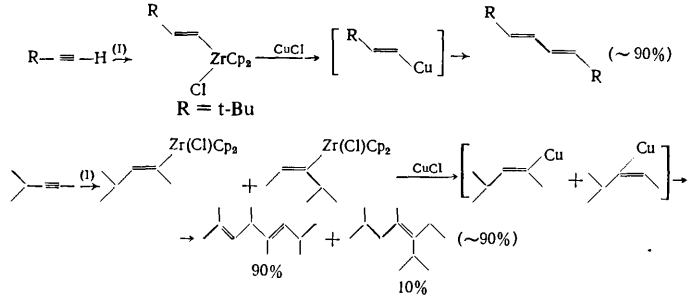


Special experiments with deuteriated alkylzirconium complexes showed that *trans*-metallation takes place predominantly with preservation of the configuration of the substituents on the carbon atom joined to the metal. This indicates a similarity between the mechanisms of *trans*-metallation and the splitting of the Zr–C bond by heteroatomic electrophilic reagents, discussed above.[43] *trans*-Metallation has been used to prepare alkyl and alkenyl complexes of a number of transition and non-transition metals.

Thus partly deuteriated *threo*- and *erythro*-alkylzirconium complexes react with $HgCl_2$ to give alkylmercury chlorides in ~50% yield with a high degree of stereoisomeric purity (≥80%).[56]



Alkenyl complexes of zirconium undergo an analogous reaction with copper salts; the configuration of the double bonds in the alkenyl groups remains unchanged. The alkenyl compounds of copper formed are extremely unstable, and decompose even at 0° to give *E,E*-conjugated dienes.[57]

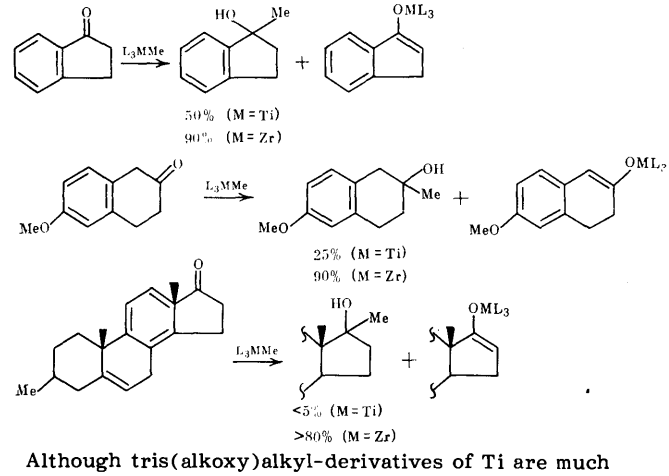


An analogous reaction is observed when copper salts are replaced by $PdCl_2$, but the yields of conjugated dienes in this case do not exceed 60%. Alkylzirconium complexes do not react with Cu and Pd salts under the conditions described.

According to Ref. 47, the reaction of alkenylzirconium complexes with $Ni(acac)_2$ also gives conjugated dienes, but no experimental details were given. A review by Schwartz[2] mentions (referring to unpublished results) that *trans*-metallation with $Sn^{IV}$ and $Zn^{II}$ compounds is possible in principle. *trans*-Metallation reactions using other transition and non-transition metals can undoubtedly be expected, and this will extend significantly the range of application of these methods in directed organic synthesis.

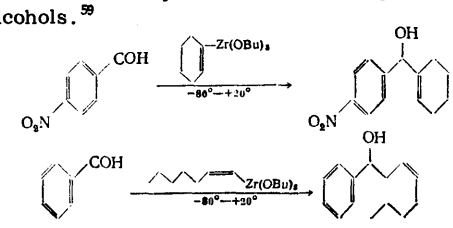
### 6. Alkoxyalkyl-complexes of Zirconium as Stable and Highly Selective Alkylating Agents

A new class of highly selective and stable alkylating agents for carbonyl compounds was recently proposed,[58–60] namely alkoxyalkyl-complexes of titanium and zirconium, obtained by the reaction of $(RO)_3MCl$ (where M = Ti, Zr) with lithium or magnesium alkyls. These reagents, particularly the Zr derivatives, are fairly stable, and differ from classical alkylating agents in their low basic strength and higher stereo- and regiospecificity, and also their selectivity, which makes it possible, for example, to alkylate aldehydes selectively in the presence of ketones with the same structure.[58,59]



Although tris(alkoxy)alkyl-derivatives of Ti are much less basic than organolithium or organomagnesium compounds, they are insufficiently nucleophilic for the successful alkylation of ketones which are readily enolised. The zirconium compounds $(RO)_3ZrR'$ successfully combine an exceptionally low basic strength with highly nucleophilic properties, so that they can be used for the selective alkylation of ketones which are readily enolised, including those containing various additional substituents. Moreover, alkoxyalkyl-compounds of titanium containing vinyl or α-branched hydrocarbon

groups decompose under the conditions of the reaction with carbonyl compounds, leading to a decrease in the yield of alkylation products. At the same time, the corresponding zirconium derivatives are more stable, and can, for example, convert aromatic aldehydes into the corresponding unsaturated alcohols.[59]



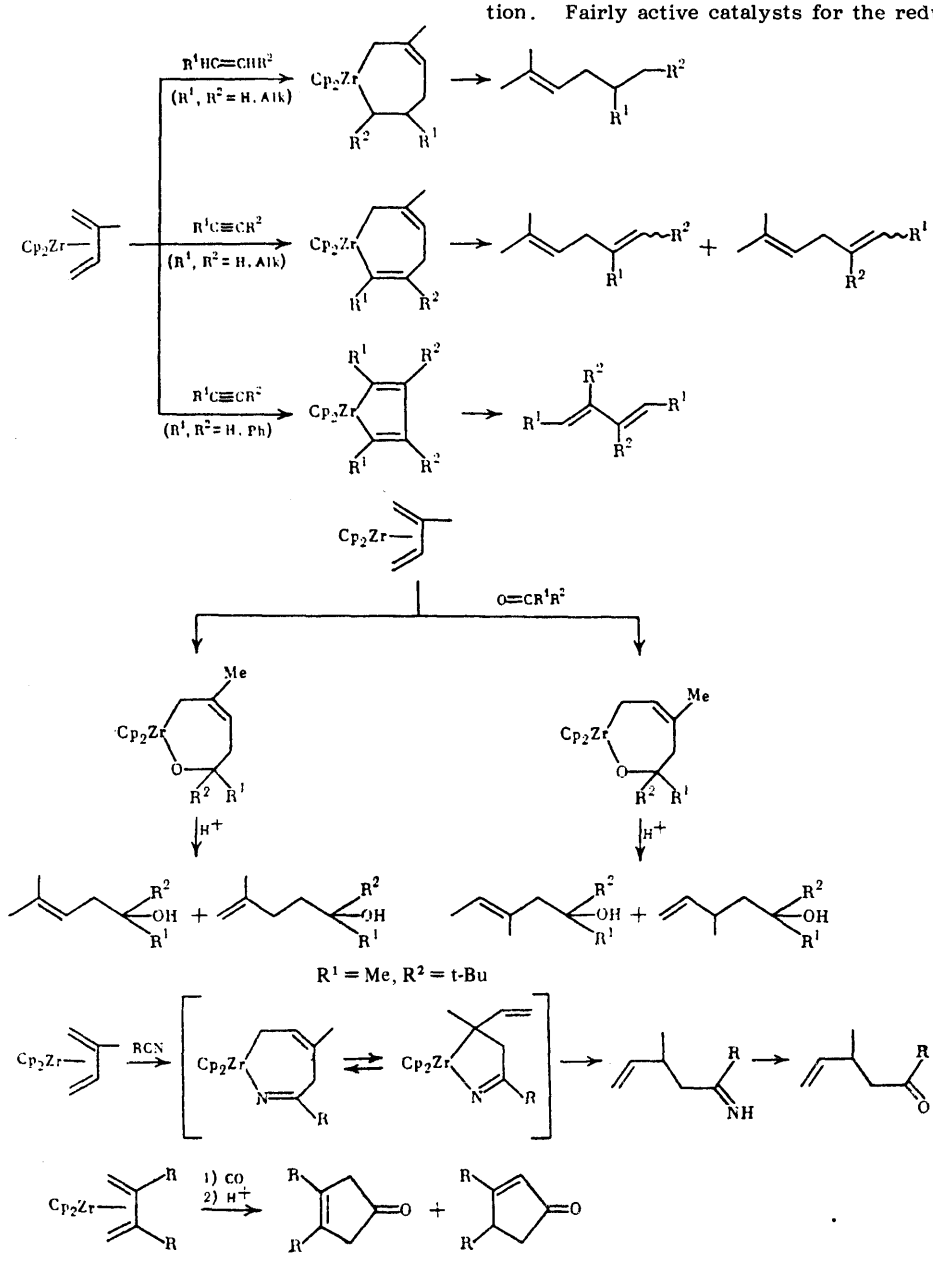
Another class of promising organozirconium reagents, synthesised in the last 2–3 years from σ,π-complexes of zirconium, should be noted. These complexes have a unique reactivity, and are being studied intensively by several groups of workers.[60–70] The most interesting reactions are given below.

## III. CATALYSIS BY ZIRCONIUM COMPLEXES

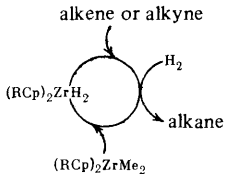
### 1. Transformations of Alkenes and Dienes, Catalysed by Zirconium Complexes

In spite of the fact that organozirconium compounds are firmly established in synthetic organic chemistry as active intermediates, their use as metal-complex catalysts in organic synthesis, apart from polymer chemistry, has only recently attracted extensive attention from research workers both in the Soviet Union and abroad.

The use of zirconium complexes as hydride-transfer catalysts has been studied in considerable detail. Thus a number of hydride complexes of zirconium(IV), fixed on activated silica gel, are highly active catalysts of the isomerisation of alkenes under mild conditions in thermodynamically equilibrium mixtures of the *cis*- and *trans*-isomers.[72] The hydrogenation of alkenes on these complexes is much slower than isomerisation. Fairly active catalysts for the reduction of alkenes

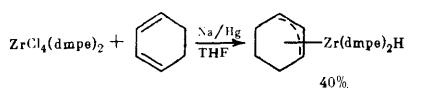


and acetylenes have been based on the zirconium complexes $RCp_2ZrR'_2$, where R' = H, Me; R = Me, $Me_2CH$, $Me_3C$.[73,74] The hydrogenation takes place by the following catalytic cycle:



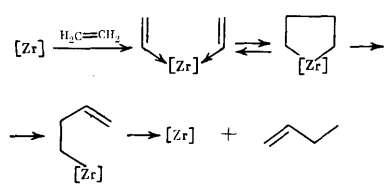

Attempts to use the optically active complexes $(R^*Cp)_2ZrR'_2$ for the asymmetric hydrogenation of the prochiral alkenes α-ethylstyrene and 2-ethylhex-2-ene were not successful. The yield of optically active hydrocarbons in these experiments did not exceed 2%, evidently because of the large distance between the chiral and reactive centres of the catalyst.[74]

High catalytic activity in hydride transfer was shown by stable low-valent zirconium complexes obtained by reducing $ZrCl_4$ with sodium amalgam in the presence of bis(dimethylphosphino)ethane (dmpe), cyclohexa-1,3-diene, or butadiene in THF solution.[75] The complexes synthesised in this way are highly active catalysts of the disproportionation of cyclohexa-2,3-dienes to cyclohexene and benzene, and of the reduction of mono0 and disubstituted alkenes and acetylenes to the corresponding alkanes.[75]



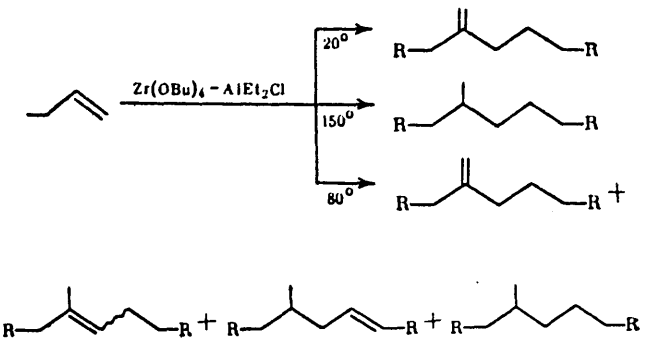

It is suggested that these processes involve the redox couples $Zr^{IV} \rightleftarrows Zr^{II}$; $Zr^{II} \rightleftarrows Zr^0$, which are the catalytically active centres in these reactions. The butadiene complex of zirconium $[Zr(C_4H_6)_2(dmpe)_2]$.dmpe catalyses the oligomerisation of various alkenes and dienes.[76]

From an an analysis of the structure of the oligomers obtained, and their distribution with respect to composition, a mechanism was proposed for the transformation of alkenes,[76] assuming the formation of five-membered metal-containing rings, which are responsible for the formation of the unsaturated hydrocarbon molecules:




The above zirconium complexes have not found extensive preparative applications, however, since they are difficult to obtain. More promising catalysts for these purposes were obtained by the reaction of accessible zirconium compounds (halides, alkoxides, acetylacetonates) with alkylhalogenoalanes. These catalysts were used to develop highly selective and effective methods for copolymerising ethylene with propylene, or converting ethylene into but-1-ene[77–79] or into higher alkenes, including α-alkenes with controlled molecular weight.[79,80]

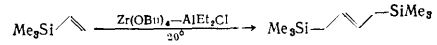
The two-component catalytic system $Zr(OBu)_4$–$AlEt_2Cl$ brings about the highly selective transformation of higher α-alkenes into unsymmetrical methylene-alkanes in high yields.[81,82] The reaction is sensitive to the structure of the original alkene and the temperature of the process. Increase in the length of the hydrocarbon group ($C_6$–$C_{10}$) in the α-alkene decreases considerably the yield of corresponding methylene-alkanes. On the other hand, with increase in the reaction temperature (100–150°), the yield of dimers increases, but dimerisation is accompanied by simultaneous isomerisation and hydrogenation of the unsaturated hydrocarbons formed.



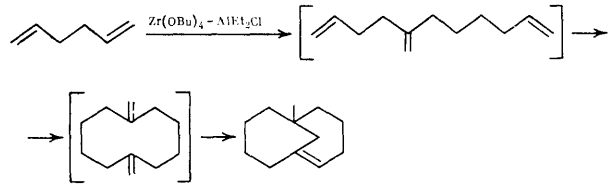




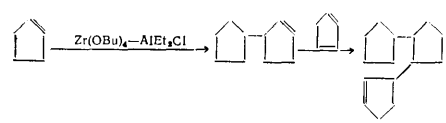
This catalytic system did not enable the authors cited to carry out the dimerisation of α-alkenes containing substituents in the α- or β-positions to the double bond. This catalyst selectively converts trimethylvinylsilane into 1,4-bis(trimethylsilyl)but-1-end.[81]




The dimerisation of hexa-1,5-diene is more complex, and gives a ~25% yield of a bicyclic hydrocarbon, identified as 6-methyl[4,4,1]bicycloundec-1-ene.[83,84]

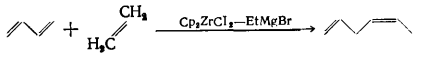



When $Et_2AlCl$ in the catalytic system is replaced by $EtAlCl_2$, it is possible to carry out the dimerisation and trimerisation of cyclic $C_5$–$C_{12}$ alkenes, whose activity in this reaction decreases in the order $C_5 > C_8 > C_7 > C_{12} > C_6$.[85]

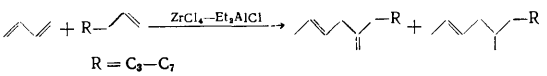



Unlike the homodimerisation of α-alkenes, the codimerisation of the latter with butadiene in the presence of zirconium complex catalysts takes place at a high temperature. Butadiene, however, having a greater coordinating power than α-alkenes, reacts with the central atom of the catalyst to form fairly stable complexes, in which the dissociation of the diene molecules and the approach and activation of the monoalkenes can take place only at a high temperature. Evidence in support of this suggestion is provided by the fact that the homodimerisation of hex-1-ene under the influence of zirconium catalysts at 20–60° is readily inhibited by the addition of butadiene.[86]

In particular, butadiene reacts with ethylene in the presence of the catalytic system $Cp_2ZrCl_2$–EtMgBr at 140–155° to give the single hydrocarbon hexa-1,4Z-diene in 20% yield.[87]

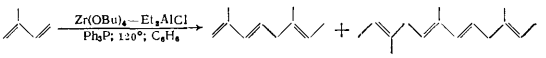


Higher α-alkenes do not react with butadiene on this catalyst, but the catalytic system $ZrCl_4$–$Et_2AlCl$ (1 : 10) makes it possible to carry out at 120° the codimerisation of butadiene with hex-1-ene, oct-1-ene, non-1-ene, and dec-1-ene to give the corresponding 2*E*,5-methylene alkenes.[80]

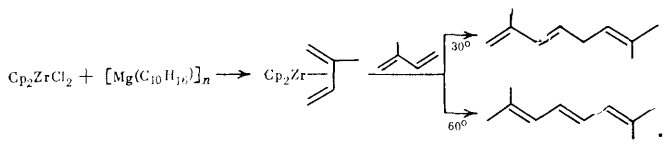


The codimerisation is accompanied by the homodimerisation of both original monomers, so that the yield of codimers does not exceed 15–20%. The mono-unsaturated codimers are evidently produced by the reaction of the initially formed 2,5-dienes with the organoaluminium component of the catalyst under the conditions of the reaction.[86]

In 1969, Japanese workers reported for the first time the possible use of the multicomponent catalytic systems $Zr(OBu)_4$–$Et_2AlCl$–$Ph_3P$ and $Zr(C_3H_5)_4$–$Et_3Al_2Cl_3$ as catalysts of the linear dimerisation of isoprene to give 2,6-dimethylocta-1,3*E*,6*E*-triene.[88,89] In addition to the latter, the reaction gave a mixture of trimers, in which the concentration of 3,6,10-trimethyldodeca-2,5,7,10-tetraene was ~90%.[90]

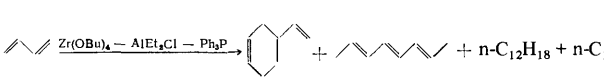


Later, more active catalysts were obtained, making it possible to increase the conversion of isoprene in this reaction to 90–95%.[91–93] The direction of the dimerisation of isoprene is changed completely by using the catalyst bis(cyclopentadienyl)isoprenylzirconium, which, depending on the reaction temperature, converts the original diene into 2,7-dimethylocta-1,3,6-triene or 2,7-dimethylocta-2,4,6-triene.[63]



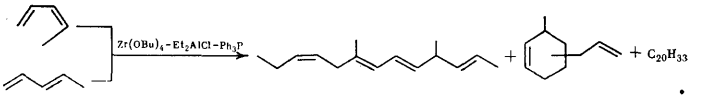
Subsequently, the authors of the present review established that three-component zirconium-containing catalysts can be used successfully for the dimerisation of other conjugated dienes with different structures.[94–97]

In the presence of the catalyst $Zr(OBu)_4$–$AlEt_2Cl$–$Ph_3P$, butadiene gives a mixture of linear and cyclic hydrocarbons consisting of 4-vinylcyclohexene, octa-2,4,6-triene, and isomeric tri- and tetramers of butadiene, differing in the positions of the double bonds.[94,95]

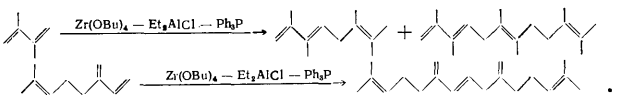


At the same time, the σ,π-complexes of zirconium formed by the reaction of $(C_8H_8)_2ZrCl_2$ with $C_3H_5MgCl$ convert butadiene with an exceptionally high selectivity into octa-1,3*E*,6*Z*-triene.[98,99]

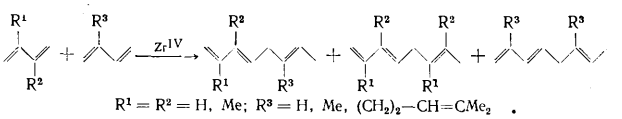
The reaction with *cis*- and *trans*-piperylenes gave 4,8-dimethyltrideca-2*E*,5*E*,7*E*,10*Z*-tetraene and a mixture of six-membered dimers and unidentified tetramers in the ratio 45 : 20 : 35.[95]



The oligomerisation of 2,3-dimethylbutadiene gives 2,3,6,7-tetramethylocta-1,3,6-triene and 2,3,6,7,10,11-hexamethyldodeca-1,3,6,10-tetraene. Myrcene is dimerised with a high selectivity to give the linear dimer 2,14-dimethyl-6-methylene-10 ethylidenepentadeca-2,7,13-triene.



The homodimerisation of farnesene gives a complex mixture of linear dimers and isomers of the original hydrocarbon.[94,95] Zirconium catalysts have made it possible to carry out the codimerisation of mono- and disubstituted conjugated dienes with different structures according to a "head-to-tail" scheme.



It is suggested[95] that the formation of linear dimers and codimers from 1,3-dienes takes place via the formation of bis-π-allyl and σ,π-allyl complexes of zirconium.

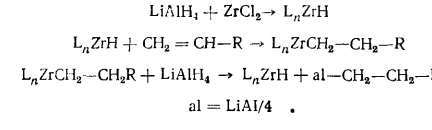
Thus of the catalysts known at present for the linear dimerisation and codimerisation of conjugated dienes, the zirconium complexes are the most universal, and can be used for the directed synthesis of polyenes with definite structures.

## 2. The Hydro- and Carbometallation of Alkenes, Dienes, and Acetylenes Under the Influence of Zirconium Catalysts

The first attempts to extend the range of application of hydroalumination using metal-complex catalysts were made by Asinger, who, in particular, used Ti and Zr compounds to convert a mixture of isomeric n-alkenes into primary alcohols by hydroalumination with tri-isobutylaluminium at 120° with subsequent oxidation of the higher organoaluminium compounds formed.[100]

The greatest progress in this field was made as a result of the discovery by Sato in the late nineteen-seventies[101,102] of the $ZrCl_4$-catalysed hydroalumination of alkenes by $LiAlH_4$ under mild conditions. Mono- and β,β'-disubstituted α-alkenes react selectively to give the corresponding lithium tetra-alkylalanates. Linear and cyclic α,β-disubstituted hydrocarbons, except cyclopentene, do not react with $LiAlH_4$ under these conditions.

According to Ref.103, the reaction takes place with the formation of intermediate hydride complexes of Zr, which hydrozirconate the alkenes, giving alkyl complexes of Zr, and subsequent *trans*-metallation leads to the regeneration of the original hydrides.



It was later established[101] that hydroalumination is catalysed not only by $ZrCl_4$ but also by $Cp_2ZrCl_2$, $VCl_4$, $Cp_2TiCl_2$, and $TiCl_4$, the last of these being the most effective catalyst. Its use made it possible to carry out the hydroalumination of alkenes with di- and trisubstituted double bonds under mild conditions, using not only $LiAlH_4$ but also $AlH_3$, $AlClH_2$, and $AlHCl_2$.

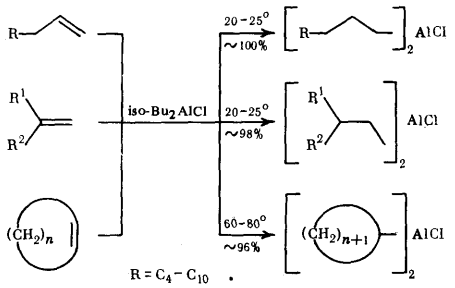
In a number of cases, however, the use of zirconium catalysts is still preferable. For example, allyl alcohols and their ethers react smoothly with $LiAlH_4$ only in the presence of Zr salts, $ZrCl_4$ is more effective for the hydroalumination of alcohols, and $Cp_2ZrCl_2$ is more effective for the hydroalumination of esters.[104,105]

The authors of the present review established[106,107] that Zr salts catalyse the hydroalumination of linear and cyclic alkenes under the influence of $(iso\text{-}Bu)_2AlH$ under mild conditions. The most effective catalysts of this reaction were found to be the mixed zirconium chloride alkoxides formed *in situ* by the reaction of $ZrCl_4$ with aliphatic alcohols or of $ZrCl_4$ with $Zr(OR)_4$. The activity of the zirconium catalysts decreases in the order: $Zr(OR)_nCl_{4-n}$ > $ZrCl_4$ > $Zr(OR)_4 \geq Cp_2ZrCl_2$.[107] The rate of hydroalumination of cycloalkenes depends on the size of the ring, and decreases in the order: cyclopentene > cyclohexene > cycloheptene > cyclododecene > cyclo-octene (Table 4).

Almost simultaneously and independently, Negishi[108] and the authors of the present review,[79,109] found that $Cp_2ZrCl_2$ catalyses the hydroalumination of mono- and disubstituted linear and cyclic alkenes under the influence of $(iso\text{-}Bu)_3Al$, $(t\text{-}Bu)_3Al$, and $(iso\text{-}Bu)_2AlCl$. The yields of the products of the hydrometallation of the alkenes are 85–99%. When $Cp_2ZrCl_2$ is replaced by $ZrCl_4$, the yields are lowered to 50%.

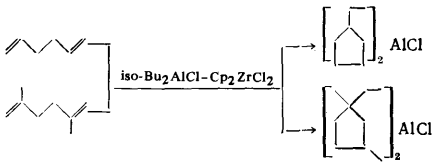
This reaction has a number of advantages over hydroalumination using dialkylaluminium hydrides, described above; in particular, it takes place under exceptionally mild conditions (0–20°) and can be carried out using alkenes containing electron-donor substituents (OH, SPh, Br), whose hydroalumination by Al hydrides is difficult.[111]

The hydroalumination of alkenes by $(iso\text{-}Bu)_2AlCl$, catalysed by $Cp_2ZrCl_2$, opens up a route to higher dialkylhalogenoalanes difficult to obtain.[109–111]

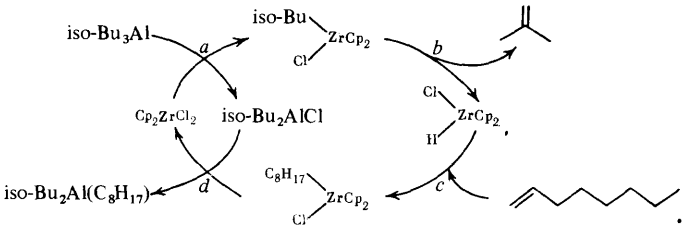



β,β′-Disubstituted alkenes are also selectively hydroaluminated by di-(n-alkyl)halogenoalanes and trialkylalanes.[112] Di-isobutylaluminium chloride reacts comparatively readily with α-alkenes at 20–25°, and with disubstituted and cyclic alkenes at 60–80°.[79]

Linear 1,5-dienes react with $(iso\text{-}Bu)_2AlCl$ in two stages. Hydroalumination takes place initially at one of the double bonds of the diene, after which intramolecular carbometallation gives the corresponding mono- and bicyclic halogenoalanes.[79]




A mechanism has been proposed for the catalysed hydroalumination of alkenes by trialkylalanes,[109,110] involving alkylation (*a*), the elimination of isobutylene (*b*), hydrozirconation (*c*), and *trans*-metallation (*d*):




This mechanism does not appear correct, however, since the regeneration of $Cp_2ZrCl_2$ from $Cp_2Zr(Cl)R$ and $(iso\text{-}Bu)_2$. .AlCl seems unlikely, because the concentration of the latter in the system is low. Moreover, according to Schwartz's data,[43] dialkylhalogenoalanes are inactive in *trans*-metallation with alkyl complexes of Zr. In the reaction conditions, under the influence of catalytic quantities of zirconium salts, trialkylalanes are probably succively split to give aluminium hydrides $R_nAlH_{3-n}$, which then bring about the hydroalumination of the alkenes or acetylenes. Evidence in support of this suggestion is provided by the fact that $(iso\text{-}Bu)_3Al$ in the presence of catalytic quantities of $ZrCl_4$ under mild conditions gives up a molecule of isobutylene, forming $(iso\text{-}Bu)_2AlH$.[79] Since groups with a normal structure are not eliminated under these conditions, the authors of the present review developed a catalytic method for obtaining higher dialkylaluminium hydrides:

$$iso\text{-}Bu_3Al \xrightarrow[30-40^\circ]{ZrCl_4} iso\text{-}Bu_2AlH + \text{(cyclohexene)} \quad \sim 98\%$$

$$iso\text{-}Bu_3Al + 2R\text{-(cyclohexene)} \xrightarrow[20^\circ]{Cp_2ZrCl_2} (R\text{-(cyclohexyl)})_2Al(iso\text{-}Bu) \xrightarrow[30-40^\circ]{ZrCl_4} (R\text{-(cyclohexyl)})_2AlH \quad \sim 96\%$$

Papers published in the last 4–5 years indicate that zirconium-containing catalysts can be used for the hydrometallation of alkenes by hydrides and hydride complexes of Mg and Zn.[111,115–117]

In particular, the hydrometallation of linear and cyclic alkenes by $ZnH_2$ has been studied in detail. The reaction is carried out at 80° in a medium of aromatic or aliphatic hydrocarbons. The most active catalyst of this reaction is $Zr(OBu)_3Cl$, obtained by the reaction of $ZrCl_4$ with $Zr(OBu)_4$. In addition to zinc dialkyls, the reaction products include metallic zinc, hydrogen, and saturated hydrocarbons; this was attributed[117] to the instability of the intermediate alkylzinc hydrides under the reaction conditions:

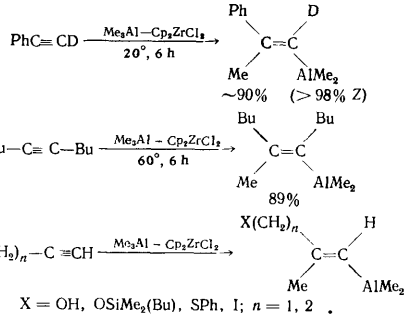
$$\text{alkene} + ZnH_2 \xrightarrow[PhMe,\ 80^\circ,\ 3\ h]{Zr(OBu)_3Cl} RZnH + R_2Zn \xrightarrow{1)\ O_2;\ 2)\ H^+} ROH \quad (D_2O \rightarrow RD)$$

$$RZnH + R_2Zn \rightarrow RZn_2H_3 + R_2Zn \xrightarrow{\Delta} RH + H_2 + Zn$$

R = alkyl, cycloalkyl

An interesting feature is that oxidation of the reaction mass with oxygen gave not the expected alkyl hydroperoxides[118] but the corresponding primary alcohols, again evidently due to the influence of the zirconium catalysts.

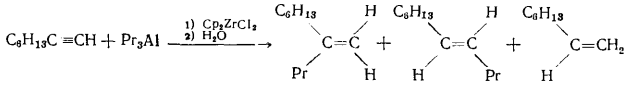
In 1978, Negishi and co-workers[110,119] carried out for the first time the $Cp_2ZrCl_2$-catalysed regio- and stereoselective *cis*-carboalumination of mono- and disubstituted acetylenes by trimethylaluminium. This reaction can be carried out with substituted acetylenes containing alkyl, alkenyl, and aromatic groups, including propargyl and homopropargyl derivatives. The carbometallation generally takes place with a high stereoselectivity, which reaches 95–100%.[110,119]




X = OH, $OSiMe_2(Bu)$, SPh, I; $n = 1, 2$ .

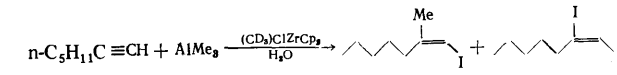
The carbometallation of monosubstituted acetylenes by $Me_3Al$, catalysed by $Cp_2ZrCl_2$, provides a simple and effective method of obtaining trisubstituted alkenes with the *cis*-configuration of the double bond, promising as synthones for the synthesis of natural products with the isoprene structure.[110]

The structure and nature of the carbometallating reagent have a much greater influence on the direction of the carboalumination of acetylene than the structure of the original acetylene. In particular, in the reaction of n-$Pr_3Al$ with oct-1-yne, the regioselectivity of the process does not exceed 70–80%, and the yield of the carbometallation products is lowered to 35–75% as a result of the simultaneous competing reaction of hydroalumination.[110]

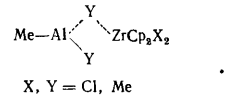



When $Pr_3Al$ is replaced by $(iso\text{-}Bu)_3Al$ or $(t\text{-}Bu)_3Al$, only hydrometallation of the acetylenes is observed. The hydrometallation of both mono- and disubstituted acetylenes can be excluded by using the $R_2AlCl$–$Cp_2ZrCl_2$ system as the carbometallating reagent.[120] The mechanism of this extremely promising reaction and the role of $Cp_2ZrCl_2$ in it are still not clear.

On the basis of recent results,[121] Negishi rejected his earlier suggestion[122] that carbometallation involves successive *trans*-metallation, carbozirconation, and *trans*-metallation. Moreover, halogen–alkyl exchange between the Al and Zr atoms, which was previously regarded as a necessary condition for carbometallation, not only is not the decisive stage, but also favours the competing reaction of hydroalumination.[121] Thus in the bimetallic system $Me_3Al$–$Cp_2$. .Zr(Cl)Me, in contrast to the reagent $Me_3Al$–$Cp_2ZrCl_2$, halogen–alkyl exchange is not observed, but the rate of the carbometallation of the acetylenes is the same in both cases. In the carbometallation of hept-1-yne by the reagent $Me_3Al$–$Cp_2Zr(CD_3)Cl$, treatment of the reaction products with $I_2$ gives a quantitative yield of a mixture of 1-iodo-2-methylhept-1*E*-ene and 3-iodohept-2*Z*-ene. The concentration of the deuteriated alkenes in these experiments did not exceed 4%.

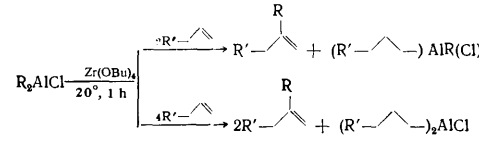



From these data, Negishi concludes that the zirconium-catalysed carboalumination of acetylenes by $Me_3Al$, at least in typical cases, involves direct carbometallation with the participation of zirconium complexes. It is suggested that the active intermediate is a bimetallic complex with the following structure:[121]

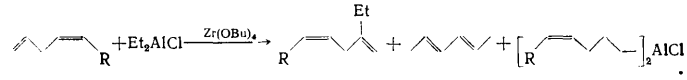



X, Y = Cl, Me

The authors of the present review were the first to establish that zirconium compounds also catalyse the carbometallation of α-alkenes by organoaluminium and organomagnesium compounds.[112 123–125] Thus the reaction of α-alkenes with dialkylaluminium halides in the presence of $Zr(OBu)_4$ leads to the selective formation of methylene-alkanes and the corresponding higher di-n-alkylaluminium halides; this can be attributed to successive carbo- and hydroalumination:[112]

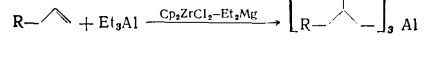



The size of the hydrocarbon group, and the presence of a localised disubstituted bond in the molecule of the original α-alkene, have no influence on the direction of the reaction, but in the last case the yield of reaction products is lower, because of the partial isomerisation of the original 1,4-diene to the 2,4-isomer.[112]



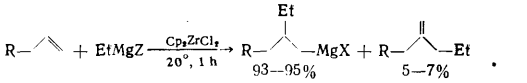

Under the conditions of this reaction, conjugated dienes polymerise, and β,β′-disubstituted alkenes, as noted above, give exclusively the hydroalumination products. The reagents with the most selective action are the dialkylhalogenoalanes.

The highest yields of carboalumination products were obtained using diethylaluminium chloride, whereas with increase in the length of the hydrocarbon group on the aluminium atom their yield decreases slightly.[112] A higher catalytic activity and selectivity of action in this reaction are shown by $Zr(OBu)_4$. In the presence of $ZrCl_4$ and $(C_5H_5N)_2ZrCl_2$, and also $TiCl_4$ and $Ti(OBu)_4$, a mixture of the products of hydro- and carbometallation, and also oligomerisation of the original alkenes, is formed, whereas $Cp_2$. .$ZrCl_2$ and $Zr(acac)_4$ were found to be completely inactive in this reaction. In the presence of an equivalent quantity of $(iso\text{-}Bu)_3Al$ or $Et_2Mg$, however, $Cp_2ZrCl_2$ catalyses the selective carboalumination of α-alkenes not only by diethylmagnesium but also by triethylaluminium. An interesting feature is that in this case the process stops at the carboalumination stage.[126,79]



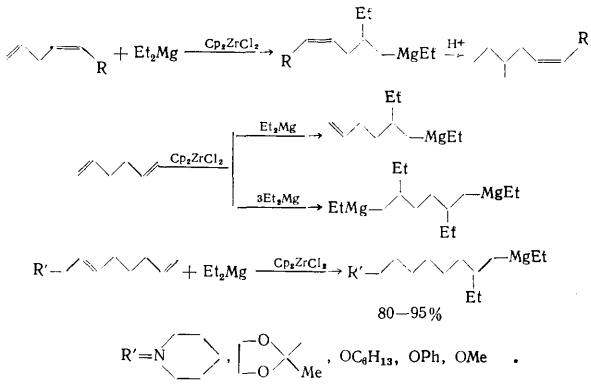

This reaction has been made the basis of a synthesis of 2-ethylhexanol from hex-1-ene and $AlEt_3$.[127]

The use of $Cp_2ZrCl_2$ made it possible to carry out under mild conditions the regioselective carbomagnesation of α-alkenes by $Et_2Mg$ or EtMgX (where X = Cl, Br, I).[125,128] Unlike the reaction of α-alkenes with $R_2AlCl$ described above, the process is not accompanied by subsequent hydrometallation. In this connection, the mechanism of formation of small quantities (5–7%) of β-alkylated alkenes under the conditions of the carbomagnesation is not yet clear. It should be noted that $ZrCl_4$ and $Zr(OBu)_4$ do not catalyse carbomagnesation; in their presence, the yield of hydromagnesation products is 3–5%. An interesting feature is that the action of $Cp_2ZrCl_2$ is completely blocked by the addition of equivalent quantities of hydrocarbons containing a triple bond or a conjugated system of double bonds.



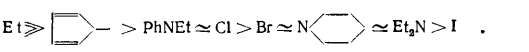
The reaction with the α-alkenes involves one ethyl group of the $Et_2Mg$ molecule or half of the ethyl groups in EtMgX, and the latter reacts much more slowly than $Et_2Mg$. This suggested that under the reaction conditions, EtMgX disproportionates to $MgX_2$ and $MgEt_2$, which is then involved in the carbomagnesation.[128]

The method described is applicable to a wide range of α-alkenes containing internal double bonds and various functional substituents, and the regioselectivity of the process remains unchanged.



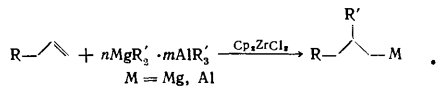
Electron-acceptor substituents on the allyl carbon atom lower considerably the activity of the double bond in carbomagnesation.

The complex $Cp_2ZrCl_2$ catalyses the carbomagnesation of α-alkenes under the influence of not only $Et_2Mg$ and EtMgX but also a number of other important Grignard reagents RMgZ, where the rate of carbomagnesation decreases in the Z order:



Compounds of the type R'OMgR, RMgSR, RMgF, and $RMgC{\equiv}CR'$ are completely inactive in carbomagnesation.[129,130] In the case of higher magnesium alkyls $R_2Mg$ (R = n-Pr, n-Bu, n-Oct), a considerable quantity of unsaturated organomagnesium compounds is formed in addition to the products of the direct carbometallation.[130]

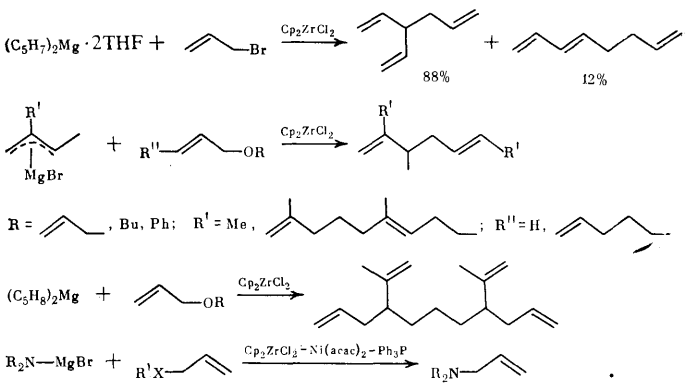
It was shown that the carbometallation of α-alkenes, catalysed by Zr salts, by bimetallic compounds in a hydrocarbon medium is possible in principle.[130]



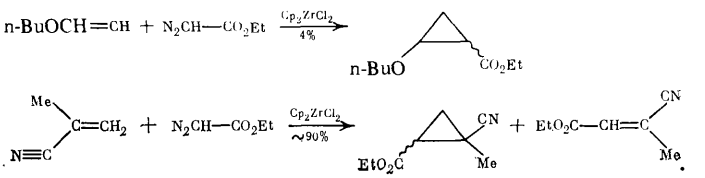
This reaction opens up extensive possibilities for the development of new effective technological carbo- and hydrometallating agents.

### 3. Other Examples of the Use of Zirconium-containing Catalysts

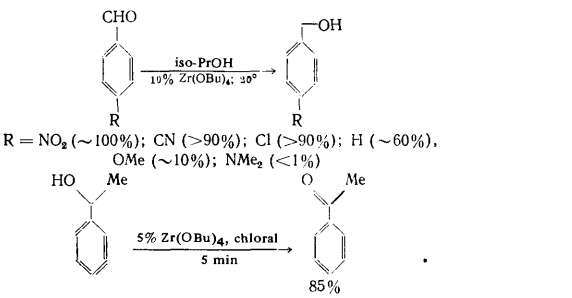
The cross-coupling of diene–magnesium complexes[131–133] and of alkenylmagnesium bromides and magnesium amides with allyl and aryl halides, catalysed by $Cp_2ZrCl_2$ and bimetallic catalysts,[132] are of undoubted interest and practical importance.



Two recent papers[134,135] describe the use of $Cp_2ZrCl_2$ to catalyse the cyclopropanation by diazoacetic ester of alkenes containing an activated double bond.



The use of zirconium tetra-alkoxides as catalysts of the Meerwein–Ponndorf–Varley reduction of carbonyl compounds or the Oppenauer oxidation of aromatic alcohols in the presence of chloral has been reported.[59]



While the present review was being prepared for publication, a number of papers on the topics of its sections were published. Thus the hydrozirconation of aliphatic and aromatic nitriles has been carried out; a heteroallyl structure

has been proposed for the complexes formed.[136] The $Cp_2ZrCl_2$–t-BuMgCl system has been proposed for the hydrozirconation of unsaturated compounds, and has been used to carry out for the first time the carbozirconation of 1,3-dienes.[137] The condensation of crotylzirconium complexes with aldehydes in the presence of $BF_3$, giving β-methylhomoallyl alcohols with predominantly the *threo*-configuration, has been described.[138] It has been shown that hydride complexes of cyclopentadienyl-zirconium can reduce the trichloromethyl groups in polychloroalkanes.[139] Studies directed towards increasing the activity of akylidene-zirconium complexes in carbonylalkenisation are continuing.[140] Zirconium(II) complexes have been used to convert ω-vinyl-1-silylalk-1-ones into zirconabicyclanes, which after treatment with CO give the corresponding α-silylbicyclopentenones.[141]

Interesting results have been obtained on hydro- and carbometallation involving zirconium-containing catalysts.[142–147]

The above results show the promising possibilities provided by the use of zirconium compounds in synthesis, including their use for the regio- and stereoselective synthesis of complex organic molecules. It is to be hoped that further studies in this field will make it possible to develop new and highly effective reagents and catalysts for organic synthesis.

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# $p\pi$-Conjugation in Aromatic Compounds of Group V and VI Elements

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The results of experimental and theoretical studies of intramolecular electronic interactions in aromatic compounds of group V and VI elements have been reviewed. The principal characteristics of their electronic structure, their geometry, and their electron-donor properties have been discussed. The possibilities provided by various methods (UV spectroscopy, NMR, PES, thermochemistry) for detecting and estimating the degree of combination of the unshared pair of electrons of the heteroatom with the $\pi$-electron system of the aromatic fragment have been analysed in detail. Quantitative estimates of the energy of $p\pi$-conjugation have been given.
The bibliography contains 240 references.

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## I. INTRODUCTION

The concept of the unshared electron pair is one of the most fundamental and widely used concepts in organic chemistry. This concept is used to explain various phenomena in the chemistry of aromatic and unsaturated compounds containing heteroatoms. The idea that the unshared electron pair (UEP) of the heteroatom interacts with the $\pi$-electron system of a neighbouring aromatic or unsaturated fragment makes it possible to explain many physical and chemical properties of the corresponding compounds. Various symbols and varied terminology are used in the scientific literature to characterise this type of intramolecular interatomic interaction. In the present review, the most widely encountered term, namely $p\pi$-conjugation, will be used.

In recent years the problem of $p\pi$-conjugation has been studied intensively by various physical methods, including photoelectron spectroscopy (PES), X-ray electron spectroscopy (XES), nuclear magnetic resonance (NMR), electron spectroscopy, etc. Together with quantum-chemical calculations, this information makes possible a deeper understanding of the nature of this interaction and enables the degree of interaction to be related to the structure and properties of the molecules. The degree of combination of the UEP of the heteroatom with the $\pi$-system determines to a large extent the electron-donor properties of compounds. The study of the electron-donor properties of aromatic compounds containing a heteroatom gives extensive information on the structure of their molecular orbitals (MO) and makes it possible in a number of cases to obtain quantitative estimates of the degree of $p\pi$-conjugation.

The present review analyses the most characteristic indications of $p\pi$-conjugation, and discusses the regular features of and differences in its manifestation in compounds of different elements for examples of simple molecules with typical compositions and structures, containing elements of groups V and VI. Particular attention has been paid to the questions of the coordination and changes in the structure of $p\pi$-conjugated molecules on complex formation.

Because of the vast amount of material, the literature in which the use of various methods to study $p\pi$-conjugated molecules is discussed has been examined selectively. Only those papers which contain information making it possible to estimate to some extent the degree of $p\pi$-conjugation have been included. The literature on the reactivity of $p\pi$-conjugated molecules (apart from their complex-forming power) is not discussed. Because of the large number of literature sources, reference is sometimes made not to an original paper but to a later review which gives references to the original work.

## II. THE STRUCTURE OF $p\pi$-CONJUGATED MOLECULES AND THEIR COMPLEXES

### 1. The Electronic Structure and Conformations of $p\pi$-Conjugated Molecules

In the valence bond (VB) method, $p\pi$-conjugation is regarded as an intramolecular donor–acceptor interaction with charge transfer.[1,2] The donor fragment is the UEP of the heteroatom, and the acceptor fragment is the $\pi$-system of an aromatic group adjoining the heteroatom. The production of this interaction is determined to a large extent by the conditions of overlap of the orbital of the UEP of the heteroatom and the $p_\pi$-orbital of the carbon atom of the aromatic fragment joined to it.

In the molecular orbital method, the extent of the production of $p\pi$-conjugation is often related to the relative contributions of the atomic orbitals, including the orbital of the UEP of the heteroatom, to the highest occupied orbitals of the molecule. Mixing of the highest occupied $\pi$-orbital of the aromatic fragment with a UEP $p_\pi$-orbital of appropriate symmetry leads to the formation of two new orbitals, whose relative positions are represented schematically in the Figure (for the anisole molecule).[3] The Figure shows that the interaction of the UEP of the heteroatom with the aromatic fragment leads to an increase in the energy of the highest occupied MO of the molecule relative to the aromatic fragment.

The energy of the $\pi$-bond produced is determined by the value of the resonance integral (MO method) or the exchange integral (VB method), and depends on the degree of overlap of the corresponding orbitals of the fragments. The overlap of orbitals is usually estimated using the overlap integral, which depends on the angle between the axis of symmetry of the $p$-component of the UEP orbital and the axis of symmetry of the $p_\pi$-orbital of the neighbouring carbon atom of the aromatic fragment.[4] Thus both the MO method and the VB method make quite definite requirements of the state of the

interacting orbitals, both in relation to their energy and in relation to their relative orientation.

Both of these methods (VB and MO) are used to interpret the experimental data obtained by different physicochemical methods. In the study of properties related to the excitation of the molecules and one-electron transitions (electronic spectra, photoelectron spectra, etc.), the MO method is usually employed.

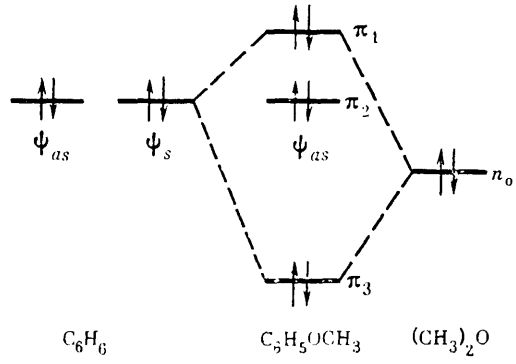



Diagram of the energy levels in the anisole molecule.[3]

The E atom in compounds of elements of group VI of the type ArER has two UEP. From the symmetry and energy of the atomic orbitals, it is assumed[3] that $p\pi$-interaction involves the UEP in the $p_z$-AO of the E atom. The extent of this interaction has been estimated[5] using the values of the resonance integrals $\beta_{E-C}$, which in compounds of the type $C_6H_5ECH_3$ decrease in the order O > S > Se > Te.

The heteroatom of tervalent compounds of group V elements has one UEP. The contribution of the $p_z$-orbital to the orbital of the UEP of compounds of group V elements can be estimated from the value θ of the C–E–C valence angle:[6]

$$p,\ \% = \frac{3\cos\theta}{\cos\theta - 1} \cdot 100$$

The average values of the valence angles θ in triaryl derivatives of group V elements, obtained by X-ray diffraction, are given below.

| Compound | N | P | As | Sb | Bi |
|---|---|---|---|---|---|
| $(C_6H_5)_3E$ | 119.6 (Ref.7) | 103.0 (Ref.8) | 100.1 (Ref.9) | — | 94 (Ref.10) |
| $(4\text{-}CH_3C_6H_4)_3E$ | 119.9 (Ref.11) | 101.7 (Ref.12) | 99.3 (Ref.13) | 97.3 (Ref.14) | 94.7 (Ref.15) |

The practically planar (θ ≅ 120°) structure of the central fragment of triarylamines indicates that the UEP of the nitrogen atom in these compounds is in the *p*-state. In the compounds of other elements, the contribution of the *p*-orbital to the orbital of the UEP is appreciably smaller, and, judging from the values of the valence angles, decreases in the order N > P > As > Sb > Bi. It may be noted that the contributions of the *p*-component to the orbital of the UEP, obtained for phosphines from the values of the valence angles, are appreciably lower than those found from the results of non-empirical calculations[16,17] or determined from an analysis of the PES by CNDO/2 calculations.[18]

Thus the orbital of the UEP in compounds of group V elements contains an appreciable contribution from the *p*-orbital, so that it is capable of reacting to some extent with a neighbouring π-system. The values of the overlap integrals of the Slater orbitals, calculated (as in Ref.19) with

**Table 1.** Geometric parameters of various amines, phosphines, ethers, and sulphides.

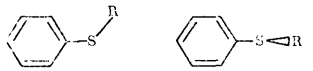
| No. | Compound | *R*(E–C), Å | θ° | Other parameters | Method | Refs. |
|---|---|---|---|---|---|---|
| (I) | $CH_3NH_2$ | 1.474 | HNH 105.9; CNH 112.0 | — | MW | [32] |
| (II) | $C_6H_5NH_2$ | 1.402 | HNH 113.1 | τ=37.5° | MW | [33] |
| (III) | $4\text{-}ClC_6H_4NH_2$ | 1.39 | HNH 137; CNH 111 | — | XRD | [34] |
| (IV) | $4\text{-}NO_2C_6H_4NH_2$ | $N_{am}$–C 1.362 | — | — | MW | [35] |
| | » | $N_{am}$–C 1.371 | 120 | φ=16° | XRD | [36] |
| (V) | $(CH_3)_2NH$ | 1.466 | CNH 108.8; CNC 112.2 | — | MW | [37] |
| (VI) | $4\text{-}FC_6H_4NHCH_3$ | — | — | τ=18° | MW | [38,39] |
| (VII) | $(CH_3)_3N$ | 1.458 | 110.9 | — | MW | [40] |
| (VIII) | $C_6H_5N(CH_3)_2$ | N–$C_{Ar}$ 1.43; N–$C_{Alk}$ 1.46 | 116 | τ=27° | MW | [41,42] |
| (IX) | $4\text{-}NO_2C_6H_4N(CH_3)_2$ | N–$C_{Ar}$ 1.36; N–$C_{Alk}$ 1.50 | 120 | φ=7.3° | XRD | [43] |
| (X) | $4\text{-}NO_2$, $2,6\text{-}Cl_2C_6H_2N(CH_3)_2$ | N–$C_{Ar}$ 1.41; N–$C_{Alk}$ 1.46 | 120 | φ=60.5° | XRD | [44] |
| (XI) | $(C_6H_5)_3N$ | 1.42 | 116 | γ=47° | ED | [45] |
| | | 1.418 | 119.6 | γ=44° | XRD | [7] |
| (XII) | $(4\text{-}CH_3C_6H_4)_3N$ | 1.419 | 119.9 | γ=42° | XRD | [11] |
| (XIII) | $CH_3PH_2$ | 1.863 | HPH 93.4; CPH 97.5 | — | MW | [46] |
| (XIV) | $C_6H_5PH_2$ | 1.839 | — | — | ED | [47] |
| (XV) | $(CH_3)_3P$ | 1.843 | 98.9 | — | MW | [40,48] |
| (XVI) | $(C_6H_5)_3P$ | 1.828 | 103 | γ=37° | XRD | [8] |
| (XVII) | $(4\text{-}CH_3C_6H_4)_3P$ | 1.832 | 101.7 | γ=42° | XRD | [12] |
| (XVIII) | $(2\text{-}CH_3C_6H_4)_3P$ | 1.835 | 102.6 | γ=45° | XRD | [49] |
| (XIX) | $[2,6\text{-}(CH_3)_2C_6H_3]_3P$ | 1.842 | 109.5 | γ=42° | XRD | [50] |
| (XX) | $[2,4,6\text{-}(CH_3)_3C_6H_2]_3P$ | 1.837 | 109.7 | γ=44° | XRD | [51] |
| (XXI)* | $[4\text{-}(CH_3)_2NC_6H_4]^{(1)}\cdot P[(C_6H_5)_2]^{(2,3)}$ | P–C 1.827; N–$C_{Ar}$ 1.280; N–$C_{Alk}$ 1.442 | CPC 102.1; CNC 120 | $\gamma^{(1)}$=37°; $\gamma^{(2)}$=55°; $\gamma^{(3)}$=38° | XRD | [52] |
| (XXII) | $(CH_3)_2O$ | 1.410 | 111.7 | — | MW | [53] |
| (XXIII) | $C_6H_5OCH_3$ | O–$C_{Ar}$ 1.361; O–$C_{Alk}$ 1.423 | 120 | φ=0° (325 K); φ=40° (523 K) | ED | [54] |
| (XXIV) | $4\text{-}FC_6H_4OCH_3$ | O–$C_{Ar}$ 1.37; O–$C_{Alk}$ 1.47 | 120 | φ=6° | MW | [55] |
| (XXV) | $1,2,4,5\text{-}(CH_3O)_4C_3H_2$ | O–$C_{Ar}$ 1.380; O–$C_{Alk}$ 1.424 | 117 | φ=0° | XRD | [56] |
| (XXVI) | $1,4\text{-}(C_2H_5O)_2C_6H_4$ | O–$C_{Ar}$ 1.377; O–$C_{Alk}$ 1.421 | 119.2 | φ=0° | XRD | [57] |
| (XXVII) | $1,4\text{-}(CH_3O)_2C_6(CH_3)_4$ | O–$C_{Ar}$ 1.379; O–$C_{Alk}$ 1.470 | 114.7 | φ=87.9° | XRD | [58] |
| (XXVIII) | $[2,4\text{-}(NO_2)_2C_6H_3]^{(1)}\cdot O[C_6H_2(t\text{-}C_4H_9)_3]^{(2)}$ | O–$C^{(1)}$ 1.35; O–$C^{(2)}$ 1.43 | 116.8 | $\varphi^{(1)}$=3.2°; $\varphi^{(2)}$=87.5° | XRD | [59] |
| (XXIX) | $(CH_3)_2S$ | 1.807 | 99.1 | — | ED | [60] |
| (XXX) | $C_6H_5SCH_3$ | S–$C_{Ar}$ 1.749; S–$C_{Alk}$ 1.803 | 105.6 | φ=45.3° | ED | [61] |
| (XXXI) | $(C_6H_5)_2S$ | 1.771 | 103.7 | — | ED | [62] |
| (XXXII) | $(4\text{-}CH_3C_6H_4)^{(1)}S(4\text{-}CH_3C_6H_4)^{(2)}$ | 1.75 | 109 | $\varphi^{(1)}$=32.5°; $\varphi^{(2)}$=35.0° | XRD | [63] |
| (XXXIII) | $[3,4\text{-}(CH_3O)_2C_6H_3]^{(1)}\cdot S[3,4\text{-}(CH_3O)_2C_6H_3]^{(2)}$ | $S\text{–}C^{(1)}_{Ar}$ 1.779; S–$C^{(2)}$ 1.764; O–$C_{Ar}$ 1.365; O–$C_{Alk}$ 1.422 | 103.1 | $\varphi^{(1)}$=3.6°; $\varphi^{(2)}$=90.9° | XRD | [64] |
| (XXXIV) | $(4\text{-}NO_2C_6H_4)^{(1)}S(C_6H_5)^{(2)}$ | 1.778(1); 1.779(2) | 104 | $\varphi^{(1)}$=2.3°; $\varphi^{(2)}$=84.3° | XRD | [64,65] |
| (XXXV) | $[4\text{-}(CH_3)_2NC_6H_4]^{(1)}\cdot S(C_6H_5)^{(2)}$ | S–$C^{(1)}$ 1.786; S–$C^{(2)}$ 1.769; N–$C_{Ar}$ 1.380; N–$C_{Alk}$ 1.449 | CSC 104.1; CNC 118.7 | $\varphi^{(1)}$=84.9°; $\varphi^{(2)}$=4.5° | XRD | [66] |
| (XXXVI) | $[4\text{-}(CH_3)_2NC_6H_4]^{(1)}\cdot S(C_6H_4NO_2\text{-}4)^{(2)}$ | S–$C^{(1)}$ 1.795; S–$C^{(2)}$ 1.780; N–$C_{Ar}$ 1.355; N–$C_{Alk}$ 1.432 | CSC 105; CNC 118.7 | $\varphi^{(1)}$=88.9°; $\varphi^{(2)}$=1.8° | XRD | [64,65] |

Symbols: *R*(E–C) is the length of the E–C bond; θ the valence angle; τ the angle between the axis of the N–$C_{Ar}$ bond and the bisector of the angle RNR (R = H, $CH_3$); φ the angle between the plane of the ring and the plane of the C–E–C angle; and γ the angle between the plane of the ring and the plane passing through the E–$C_{Ar}$ bond and the axis of the UEP. Methods: MW = microwave spectroscopy, ED = electron diffraction, XRD = X-ray diffraction. The geometric parameters for identical atoms and groups, obtained by X-ray diffraction, have been averaged.

*Here and subsequently the superscript in brackets gives the number of the aromatic ring.

allowance for the values of the C–E–C angle in compounds of the type $(C_6H_5)_3E$, decrease in the order: N–C > P–C > As–C > Sb–C > Bi–C (0.185, 0.119, 0.093, 0.063, 0.040 respectively). The angles of rotation of the aryl fragments about the E–C bond were not taken into account, since they have similar values for all triphenyl and tri-*p*-tolyl derivatives of group V elements ($\gamma$ = 37–47°, Table 1).[7–15]

The conformation of molecules of the type $C_6H_5ER$ is determined to a large extent by the competition between two factors: $p\pi$-conjugation (which is a maximum for the planar conformation (A), $\phi$ = 0°) and steric hindrance (which is a minimum for the orthogonal conformation (B), $\phi$ = 90°).



(A) (B)

Depending on the contributions of these effects determining the barrier to the rotation of the ER group relative to the ring, an effective conformation with an angle of $0° \leq \phi \leq 90°$, and an equilibrium between planar and orthogonal conformers, may be produced. From data on the dipole moments (DM) and Kerr constants of anisole[20,21] and thioanisole[22] it was concluded that these compounds show conformational uniformity; the angles $\theta$ are 18°[20] and 23°[22] respectively.

At the same time, data obtained from an analysis of the temperature dependence of the Raman spectra of anisole indicate[23] that the system contains the conformers (A) and (B). The same conclusion was reached in a study of the PES of anisole;[24] the difference in the energies of the conformers (B) and (A) was estimated as 1.3 kcal mole$^{-1}$. From the observed splitting of the first band in the PES of a series of compounds of the type $C_6H_5SR$,[25] it was concluded that they show conformational non-uniformity in the gas phase. Estimation of the concentration of the conformers from the ratio of the intensities of the components of the complex PES band showed that the proportion of the planar conformer decreases with increase in the volume of the alkyl substituent R, and has the values 0.90, 0.40, 0.15, and 0.05 for R = $CH_3$, $C_2H_5$, iso-$C_3H_7$, and t-$C_4H_9$ respectively. Approximately the same ratio of conformers for the compounds $C_6H_5SR$ was obtained from UV and NMR spectroscopy.[26,27] At the same time, other authors[28] consider that the analysis of the PES of these compounds does not indicate unambiguously whether increase in the volume of the alkyl group leads to a gradual increase in the angle $\phi$ or displaces the conformational equilibrium (A) $\rightleftarrows$ (B).

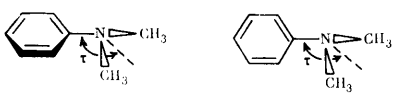
New classes of conformationally non-uniform alkylaromatic and unsaturated compounds of group V and VI elements have been described in recent papers. These include alkylaromatic compounds of selenium and tellurium,[3,29,30] alkyl phenyl ethers and sulphides containing different substituents,[3,30,31] and compounds of the type $(C_6H_5)_nPR_{3-n}$.[26,31] The difference in the energies $\Delta E_{A-B}$ of the conformers (A) and (B) is generally small. Thus for the compounds $C_6H_5SR$, the values for R = $CH_3$, $C_2H_5$, iso-$C_4H_9$, and t-$C_4H_9$ are –3.1, –1.4, –1.0, and 4.6 kJ mole$^{-1}$.[31] The comparatively small difference in the energies of the planar and orthogonal conformers of these compounds is apparently one of the reasons why they cannot be distinguished by certain methods. The methods examined below for estimating the energy of the $p\pi$-conjugation of aromatic compounds relate to the averaged characteristics of the geometry, and are interpreted in terms of the average value of the angle $\phi$.

## 2. The Geometry of the Molecules of Aromatic Compounds of Group V and VI Elements

Intramolecular $p\pi$-interactions are reflected in the structural parameters of molecules. This question can be examined for the compounds of nitrogen and phosphorus (group V) and oxygen and sulphur (group VI).

Table 1 gives the bond lengths, valence angles, and various other structural parameters of the key fragments of molecules, obtained by microwave spectroscopy, gas-phase electron diffraction, and the X-ray diffraction study of crystals. The data for various aliphatic compounds are given for comparison. These are mainly the most reliable results obtained in recent years. Primary, secondary, and tertiary aliphatic amines ((I), (V), and (VII)) have a pyramidal configuration with an average value of the valence angle of the heteroatom ($\theta$) of 110–111°. The pyramidal character of aromatic amines ((II)–(IV), (VI), (VIII)–(XII)) is much less marked, and the average value of the valence angle of the heteroatom is greater and for a number of compounds reaches 120°, that is the amino-group has the planar conformation ($sp^2$ hybridisation of the nitrogen atom), most favourable for $p\pi$-conjugation with the appropriate orientation of the aryl fragment.

The values of the angle $\phi$ in Table 1 show that in compounds (IV) and (IX) the ring and the amino-group are almost coplanar. The pyramidal (in the gas phase) molecules of aniline, N-methylaniline, N,N-dimethylaniline, and anilines containing substituents in the ring have the conformation (C), favourable for $p\pi$-conjugation.[33,38,39,41,42,67,68] For the molecule $C_6H_5CH(CH_3)_2$, the conformation (D) predominates.[69]



(C); $\gamma$ = 90° (D); $\gamma$ = 0°

The influence of $p\pi$-conjugation is reflected not only in the valence angles and the conformation of the molecules but also in the E–C bond lengths. Thus the $N-C_{Ar}$ bond length in $p\pi$-conjugated molecules is appreciably shorter than $N-C_{Alk}$ (see Table 1). The bond length depends not only on the degree of double bond character but also on a number of other factors, such as the nature of the hybridisation of the orbitals and the electronegativities of the atoms forming the bond.[70] The increase in the $N-C_{Ar}$ bond length when there is steric inhibition of $p\pi$-conjugation or when aromatic amines are protonated (see below) shows, however, that the difference in the $N-C_{Ar}$ and $N-C_{Alk}$ bond lengths is determined chiefly by $p\pi$-conjugation.

In this connection, it is of interest to examine the structure of 2,6-dichloro-4-nitro-N,N-dimethylaniline (X).[44] In this molecule, for steric reasons, the $p\pi$-conjugation of the dimethylamino-group is prevented to a considerable extent; the angle between the plane of the amino-group and the ring is 60.5°. The $N_{am}-C_{Ar}$ bond length is 1.41 Å, which is much greater than in compound (IX) (1.36 Å) or in 3,5-dichloro-4-nitroaniline (1.37 Å).[44]

Gas-phase electron diffraction[45] has shown that the molecule of triphenylamine (XI) is slightly pyramidal ($\theta$ = 116°). X-Ray diffraction[7,11] has shown that the amine fragment of the crystalline amines (XI) and (XII) is planar ($\theta \cong 120°$). For steric reasons, however, triarylamines cannot have the conformation most favourable for $p\pi$-conjugation, with the ring and the amino-group coplanar. For triphenylamine, the values obtained for the angle $\gamma$ are 47° from electron diffraction,[45] 44° from X-ray diffraction,[7] and 62° from data on the Kerr effect.[71]

In the molecules of crystalline *ortho*- and *para*-phenylenediamine, the amino-group has a pyramidal structure.[72,73] The non-planar structure of *ortho*-phenylenediamine ($\theta$ = 112.7°) was attributed[72] to the mutual repulsion of the two closely situated UEP and the location of these UEP on different sides of the plane of the ring. The presence of intermolecular H-bonds of the type N–H...N in *ortho*- and *para*-phenylenediamine crystals may influence the geometry of the amino-group.

The degree of pyramidal character of the aromatic phosphines (XVI)–(XXI) is lower than that of the aliphatic phosphines (XIII) and (XV). The valence angle of the phosphorus atom is ~102–103° for the sterically non-overcrowded triarylphosphines (XVI)–(XVIII) and (XXI), which corresponds to approximately *sp* hybridisation of the UEP of the phosphorus atom and indicates that the UEP of the phosphorus atom can be involved in $p\pi$-conjugation.[19] The angles of rotation of the rings ($\gamma$) for the triarylphosphines (XVI)–(XXI) differ little from the corresponding angles of rotation for the triarylamines (XI) and (XII) and is ~40°. From data on the Kerr effect, the angle $\gamma$ for triphenylphosphine in solution is 59°.[71]

The steric effects of phosphorus-containing ligands in transition metal complexes have been analysed.[74] The steric effects of phosphines increase in the order: $(CH_3)_3P$ < $(C_2H_5)_3P$, $(C_3H_7)_3P$ < $(C_6H_5)_3P$, $(iso\text{-}C_4H_9)_3P$ < $(iso\text{-}C_3H_7)_3P$ < $(C_6H_{11})_3P$ < $(t\text{-}C_4H_9)_3P$ < $[2,4,6\text{-}(CH_3)_3C_6H_2]_3P$. The greatest steric effect is observed for trimesitylphosphine. The introduction of $CH_3$ groups in positions 2 and 6 of each ring of triphenylphosphine leads to a sharp increase (to 109.5°) in the valence angle of the phosphorus atom both in the crystalline phase (XIX) and (XX) (see Table 1) and in solution.[75] The average value of the angle $\gamma$ differs little from that for triphenylphosphine. An increase in the valence angle of the heteroatom is also observed when two $CH_3$ groups are introduced in the *ortho*-positions of each ring of triphenylarsenic,[76] triphenylantimony,[77] and triphenylbismuth.[78]

The conformation of phenylphosphines is not yet clear. According to electron diffraction data, the molecules of $C_6H_5PH_2$ and $C_6H_5PCl_2$ have the conformation (D) with angle $\gamma$ = 0°,[47,69,79] and the $C_6H_5PF_2$ molecule has a conformation with an angle $\gamma$ = 31°.[80] Data on the Kerr effect do not make it possible to reach definite conclusions about the conformation of dialkylarylphosphines in solution.[31,81–83] Recent data[26,31] indicate that an equilibrium between the conjugated (C) and non-conjugated (D) conformers is established in solution. The data in Table 1 show that the P–$C_{Ar}$ bond is shorter than P–$C_{Alk}$, but the difference is much smaller than in the case of amines; this question will be examined below.

The C–E–C valence angle in the sterically non-overcrowded aromatic ethers (XXIII)–(XXVI) and sulphides (XXX)–(XXXVI) is much larger than in the corresponding aliphatic compounds (XXII) and (XXIX).[69] The crystalline aromatic ethers (XXIII)–(XXVI) have the planar conformation (A) ($\phi$ = 0°) favourable for $p\pi$-conjugation. In the gas phase at a temperature of 325 K, anisole has an almost planar conformation; with increase in temperature to 523 K, the geometry of the anisole molecule changes considerably, and the angle $\phi$ increases to 40°.[84] The lower ability of sulphur and selenium atoms, compared with oxygen, to take part in $p\pi$-conjugation leads to much larger values of the angle $\phi$ in thioanisole (XXX) (45.3°) and selenoanisole (40°).[84] Data on the Kerr effect indicate that anisole,[20] thioanisole,[22] and selenoanisole[85] have non-planar structures, and that the angle $\phi$ increases in the order indicated. When electron-acceptor substituents (for example $NO_2$) are introduced into the *para*-position, the $p\pi$-conjugation of the O, S, and Se atoms with the ring increases, and the angle $\phi$ decreases.[20,22,85]

The coplanarity of the ring and the methoxy-group may be destroyed by steric factors. *para*-Dimethoxybenzene[86] and *para*-diethoxybenzene (XXVI) have planar structures. The introduction of four bulky substituents, $CH_3$ (XXVII), and also Cl and Br,[87] into the 2,3,5,6-positions of the ring displaces the methoxy-groups from the plane of the ring ($\phi$ = 84–88°); the valence angle of the oxygen atom decreases to 114.5°, and the $p\pi$-conjugation is destroyed.[88] The conformation of compounds containing two methoxy-groups in the *ortho*-position to one another apparently depends on the state of aggregation. In the crystalline state, the molecules are planar (XXV), but in the gas phase, one of the methoxy-groups is coplanar with the ring, but the second is not.[86] The conformation of these molecules in solution is not clear.[89,90]

A coplanar arrangement of the two phenyl rings and the plane of the CEC angle in diphenyl ether and diphenyl sulphide is impossible, for steric reasons. If one of the rings is coplanar with the plane of the CEC angle ($\phi$ = 0°), the second ring forms an angle $\phi$ = 70–90° with this plane, (XXVIII) and (XXXIII)–(XXXVI). The introduction of an electron-acceptor substituent into one of the rings of diphenyl sulphide (XXXIV) facilitates $p\pi$-conjugation of the substituted ring, as indicated by the value of the angle $\phi^{(1)}$ = 2.3°, whereas the angle $\phi^{(2)}$ for the non-substituted ring is 84.3°. On the other hand, the introduction of an electron-donor substituent into one of the rings (XXXV) leads to coplanarity of the CSC group and the non-substituted ring. In the diaryl sulphide (XXXVI), the CSC plane is coplanar with the ring containing the nitro-group ($\phi^{(2)}$ = 1.8°) and makes an angle of 68.9° with the ring containing the dimethylamino-group. If the substituents are identical, the angles $\phi^{(1)}$ and $\phi^{(2)}$ may be similar (XXXII) or different (XXXIII); this apparently depends on the packing conditions in the crystals. In this connection it should be noted that electron diffraction[62] did not make it possible to conclude that diphenyl sulphide has a definite conformation in the gas phase. This agrees with the idea that molecules of the type $Ar_2E$ are non-rigid. The two equivalent aryl rings can rotate relative to one another about the E–$C_{Ar}$ bonds. A non-rigid structure has been proposed for diphenyl ether.[91,92]

### 3. Changes in the Structure of Molecules on Complex Formation

The extent of the rearrangement of the molecules of electron donors on complex formation depends on the type of complex formed and the strength of the electron acceptor. Complexes with compounds of group III elements will be examined, since in the interaction with these acceptors, the geometry of aromatic compounds containing a heteroatom undergoes a rearrangement leading to breakdown of the $p\pi$-conjugation.[93] Breakdown of the $p\pi$-conjugation in aromatic amines and phosphines has also been observed when a H-bond is formed with strong carboxylic acids and on protonation.[19,94,95]

Gillespie's theory[96] predicts that when a complex is formed, the valence angle of the heteroatom of an acceptor should decrease, and the length of the bonds should increase. On the other hand, the valence angle of the heteroatom of a donor should increase, and the length of the bonds should decrease. The changes in the geometry of trimethylphosphine on complex formation with $BH_3$ (Table 2) agree with this prediction. The differences in the valence angles and bond lengths of the original trimethylphosphine and triphenylphosphine practically disappear when complexes are formed with $BH_3$ (Table 2). The geometry of the $R_3P$ frag-

ments of trimethylphosphine and triphenylphosphine in the complexes is close to that of the $R_3P$ fragments in phosphine oxides. All this indicates that the differences in the geometry of trimethylphosphine and triphenylphosphine are related to the $p\pi$-conjugation in the molecule of the latter. This applies particularly to the P–C bond length. In tetravalent phosphorus compounds there are no differences in the P–$C_{Ar}$ and P–$C_{Alk}$ bond lengths.[102]

**Table 2.** Geometric parameters of various phosphines, phosphine oxides, and complexes with $BH_3$.*

| Compound | θ, ° | $R$(P-C), Å | $R$(P-B) or $R$(P-O), Å | Method | Refs. |
|---|---|---|---|---|---|
| $(CH_3)_3P$ | 98.9 | 1.843 | — | MW | [48] |
| $(C_6H_5)_3P$ | 103.0 | 1.828 | — | XRD | [8] |
| $(CH_3)_3P\cdot BH_3$ | 105.0 | 1.819 | 1.901 | MW | [97] |
| $(C_6H_5)_3P\cdot BH_3$ | 106.3 | 1.820 | 1.917 | XRD | [98] |
| $(CH_3)_3PO$ | 104.1; 106.0 | 1.809; 1.81 | 1.476; 1.48 | ED | [99, 100] |
| $(C_6H_5)_3PO$ | 106.2 | 1.82 | 1.49 | XRD | [101] |

*For symbols see Table 1.

Aromatic phosphines, particularly triphenylphosphine, are widely used as ligands in transition metal complexes. Many of these complexes have been studied by X-ray diffraction. The value of the C–P–C angle of the phosphorus atoms in both aliphatic and aromatic phosphines in transition metal complexes varies over a wide range (100–108° in triphenylphosphine); here, an important role is played by the strength of the coordinate bond and steric effects.[74, 103]

Aliphatic amines undergo slight rearrangement on complex formation, and, in contrast to the case of aliphatic phosphines, the nature of the rearrangement does not agree with Gillespie's theory. Thus the C–N–C angle in the molecule of trimethylamine (110.9°) decreases in the complexes with compounds of group III elements to 108–111°, and the N–C bond length increases from 1.458 Å to 1.47–1.49 Å. The reasons for this anomaly are discussed, for example, in Refs. 104–106.

**Table 3.** N–C bond lengths in protonated ($R_1$) and non-protonated ($R_2$) aromatic amines.

| Compound | $R_1$, Å | $R_2$, Å |
|---|---|---|
| $4\text{-}NO_2C_6H_4NH_2\cdot HCl$ | 1.472 [110] | 1.371 [36] |
| $1,2\text{-}(NH_2)_2C_6H_4\cdot HCl$ | 1.460 [111] | 1.391* [111] |
| $1,2\text{-}(NH_2)_2C_6H_4\cdot 2HBr$ | 1.445 [112] | 1.407 [72] |
| $1,4\text{-}(NH_2)_2C_6H_4\cdot 2HCl$ | 1.463 [113] | 1.408 [73] |
| $(C_6H_5)_2N(CH_2)_2\overset{+}{N}\overset{C_6H_5}{\underset{C_6H_5}{\overset{CH_3}{<}}}\ I^-$ | $N-C_{Ar}$ 1.497; $N-C_{Alk}$ 1.502 [114] | $N-C_{Ar}$ 1.414*; $N-C_{Alk}$ 1.451 [114] |

*N–C bond length in the neutral amino-group of the complex.

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

There are no published data on the structure of complexes of aromatic amines with compounds of group III elements, but X-ray diffraction studies of transition metal complexes indicate that there is considerable rearrangement of aromatic amines on complex formation. As in the case of phosphines, the differences in the geometry of aliphatic and aromatic amines disappear on complex formation. The C–N–C valence angles decrease from 120° in the free aromatic amine to tetrahedral in a complex, and the N–$C_{Ar}$ bond length increases sharply, becoming equal to the N–$C_{Alk}$ bond length. Similar structural changes were observed for the molecule of N,N-dimethylaniline on complex formation with copper compounds,[107] for aniline and 4-toluidine in their complexes with nickel compounds,[108] and for 4-toluidine in its complex with $CdI_2$.[109]

Table 3 gives the N–$C_{Ar}$ bond lengths in protonated aromatic amines and the N–$C_{Ar}$ bond lengths for the corresponding neutral molecules. Protonation or methylation of the amino-group leads to a considerable increase in the N–$C_{Ar}$ bond length to 1.45–1.50 Å, that is to a value characteristic of N–$C_{Alk}$ bonds. The observed effect is evidently related to the breakdown of $p\pi$-conjugation on protonation of the aromatic amines.

## III. THE ELECTRON-DONOR PROPERTIES OF AROMATIC COMPOUNDS OF GROUP V AND VI ELEMENTS

### 1. π-Donor Properties

Donors having a heteroatom with an UEP and a system of π-bonds can be divided into two groups. A characteristic feature of the molecules of one group is that the UEP of the corresponding heteroatom is not joined directly to the π-system of the molecule (pyridine, aryl ketones, etc.). In the molecules of the second group, the UEP of the heteroatom is included in the conjugated system (furan, thiophene, anisole, etc.).

The donors of the two groups behave differently towards different acceptors. The first group of donors, in their reactions with σ-acceptors ($I_2$, ICl, etc.) and ν-acceptors ($BF_3$, $AlCl_3$, $SnCl_4$, etc.) show the properties of *n*-donors, that is the intermolecular bond involves the free UEP of the heteroatom.[93] In their reaction with π-acceptors, the donors of the first group show π-donor properties.[93] In compounds of the second group, the UEP of the heteroatom is not free, but is involved in $p\pi$-conjugation. These compounds are weaker *n*-donors than the corresponding aliphatic compounds (see below). This is illustrated by the compounds furan and thiophene, which do not show *n*-donor properties and which form π-complexes not only with π-acceptors but also with σ- and ν-acceptors.[115,116] The symmetry and energy of the MO of analogues of furan have been discussed.[117]

The electronic spectra of complexes of aromatic and heteroaromatic π-donors with π- and σ-acceptors may contain two (and sometimes more) charge-transfer bands, as a result of the participation in complex formation of not only the HOMO but also lower-lying orbitals of the π-donor. As shown in the Figure, transitions from the $\pi_1$ and $\pi_2$ orbitals of the donor molecule are most probable.[115,118–122] The relative arrangement of the energy levels of the π-donor (see Figure) is determined by a number of factors, and primarily by the energies of the UEP of the heteroatom and the π-system.[3] The structure of the MO in aromatic compounds of group VI elements, of the type $C_6H_5ECH_3$, $XC_6H_4ECH_3$, $XC_6H_4ER$, etc. (from the electronic spectra of charge-transfer complexes of tetracyanoethylene and iodine and quantum-chemical calculations) has been discussed in a number of papers (see Refs. 3 and 123–126 and references therein).

The complexes of aromatic compounds of group V elements with π-acceptors (except nitrogen compounds) have been less extensively studied, and the available data are somewhat contradictory. The question of whether the complexes of aromatic amines with nitrobenzenes are π-complexes, *n*-com-

plexes, or complexes with an H-bond has not yet been resolved.[127] It is not clear whether the $p\pi$-conjugation is destroyed when $I_2$ forms complexes with aromatic amines, that is whether the molecular compounds formed are $n,\sigma$- or $\pi,\sigma$-complexes.[93,128]

Complex formation by aromatic amines with various $\pi$-acceptors is accompanied by chemical reactions. The latter often depend on the conditions of the experiment. Low temperatures and inert solvents stabilise $\pi,\pi$-complexes.[129–132] Triarylphosphines react with tetracyanoethylene in dichloroethane in the same way as amines, that is $\pi,\pi$ complexes are formed first, after which reactions take place.[133] A similar study[134] of the complexes of $(C_6H_5)_3N$, $(C_6H_5)_3P$, and $(C_6H_5)_3$. .As with tetracyanoethylene in chloroform, however, led to the conclusion that the complexes formed are stable. As in the case of the complexes of tetracyanoethylene with aromatic ethers and sulphides, the spectra of these complexes contain two charge-transfer bands, which were assigned to transitions from the two highest MO of the donor to the LUMO of the acceptor.

Since the chief characteristics of the charge-transfer bands in the spectra of charge-transfer complexes are determined by the highest occupied orbitals of the donor molecule, it is natural to look for correlations between the energies of these bands ($h\nu$) and the ionisation potentials (IP) of the donors. For many classes of compound of group VI[3,115,119,128,131,135,136] and V [131,133,134] elements, a linear correlation has been observed between $h\nu$ and IP. This relationship has been widely used to determine IP from $h\nu$ data for charge-transfer complexes. The question of the range within which a linear correlation is observed between $h\nu$ and IP has been examined.[1,93,137]

The participation of several MO of a donor in electron transitions has been used[138–140] to explain the differences in the structures of the complexes formed, for example the "longitudinal" and "transverse" orientation of the tetracyanoethylene molecule relative to the phenyl ring in complexes with substituted benzenes. The relative orientation of the molecules of the donor and acceptor in $\pi,\pi$- and $\pi,\sigma$-complexes, as in complexes of other types, is determined to a large extent by the principle of maximum overlap of the interacting orbitals.[1,93] Of the two highest MO of aromatic compounds containing a heteroatom, only one contains a contribution from the UEP of the heteroatom (see Figure) and hence is localised in the region of the $E-C_{Ar}$ bond. The second orbital of $\pi$-symmetry is localised in the hydrocarbon fragment.[117,121] Different orientations of the acceptor molecule in the complex are possible, depending on which of these two orbitals overlaps the orbital of the acceptor. Evidence in support of this approach is provided, for example, by the results of an X-ray diffraction study of the charge-transfer complex of fluoranil with N,N-dimethylaniline.[141] In this case, two orientations of the fluoranil molecule were detected: in one of them, the ring of the acceptor is positioned directly above the phenyl ring of the donor, and in the other it is directly above the dimethylamino-group; judging from the distances between the donor and acceptor, the interaction in the latter case is stronger than in the former.

The energy of formation of $\pi,\pi$-complexes is generally low (~1–3 kcal mole$^{-1}$),[119,129,132] and the extent of charge transfar in the ground state of the complex does not exceed ~0.05;[119,120] complex formation in these systems is not accompanied by a significant rearrangement of the molecules of the donor and acceptor.[142–144] This makes it possible to use the electronic spectra of charge-transfer complexes to study intramolecular electronic interactions in organic and organometallic compounds.[145]

### 2. *n*-Donor Properties. The Determination of the Energy of $p\pi$-Conjugation by the Method of Complex Formation

On $\pi$-complex formation, aromatic compounds containing a heteroatom do not undergo appreciable rearrangement; the system of MO formed as a result of $p\pi$-conjugation is preserved. A fundamentally different picture is observed in the reaction of these compounds with strong electron acceptors (the halides of group III elements, strong carboxylic acids, etc.). The donor–acceptor bond is formed by the UEP of the heteroatom of the donor and an unoccupied orbital of the acceptor. The $p\pi$-conjugation is destroyed, the MO system of the original aromatic compound breaks down, and and an MO system characteristic of the aromatic fragment of the molecule is produced. A good illustration of this is provided by the changes in the electronic spectra of aromatic amines, ethers, phosphines, and sulphides on complex formation with strong acceptors (see below)

Some physicochemical properties and geometric characteristics (see above) of complexes of strong acceptors with aromatic and corresponding aliphatic *n*-donors are similar. These are the properties which are determined by the strength of the donor–acceptor bond ($-\Delta H_{DA}$) and the magnitude of the charge transferred from the donor to the acceptor. One such parameter is the dipole moment of the donor–acceptor bond ($\mu_{DA}$) and (other conditions being equal) the dipole moment of the complex as a whole ($\mu_c$), and also the extent of charge transfer from the donor to the acceptor $\mu_{DA}/er_{DA}$ ($r_{DA}$ is the length of the donor–acceptor bond), determined from the value of $\mu_{DA}$. Some examples are given in Table 4. The dipole moments of the complexes of the halides of boron, aluminium, and gallium with aliphatic and aromatic *n*-donors (amines, ethers, phosphines, sulphides) differ little from one another.[19,93,146]

Table 4. Dipole moments ($\mu_c$, D) and enthalpies of formation of the complexes $D.AlBr_3$($-\Delta H$, kcal mole$^{-1}$).[19,146] *

| D | $\mu_c$ | $-\Delta H$ | $\Delta\Delta H$** | D | $\mu_c$ | $-\Delta H$ | $\Delta\Delta H$** |
|---|---|---|---|---|---|---|---|
| $Alk_2O$ | 7.2 (av) | 23.3 (av) | — | $Alk_3N$ | 8.6 (av) | 32.3 (av) | — |
| $C_6H_5OCH_3$ | 7.00 | 15.9 | 7.4 | $C_6H_5N(CH_3)_2$ | 8.68 | 24.2 | 8.1 |
| $(C_6H_5)_2O$ | 7.29 | 12.0 | 11.3 | $(C_6H_5)_2NCH_3$ | 8.01 | 17.4 | 14.9 |
| $Alk_2S$ | 7.6 (av) | 17.5 (av) | — | $Alk_3P$ | 10.2 (av) | 32.2 (av) | — |
| $C_6H_5SCH_3$ | 7.00 | 13.1 | 4.4 | $C_6H_5P(C_3H_7)_2$ | — | 27.7 | 4.5 |
| $(C_6H_5)_2S$ | 7.55 | 10.2 | 7.3 | $(C_6H_5)_3P$ | 10.0 | 21.3 | 10.9 |

*Some of the $-\Delta H$ values have been refined by the present authors.
**See the text for the significance of $\Delta\Delta H$.

A characteristic feature of donor–acceptor complexes is the relationship between the magnitude of the transferred charge and the energy of the donor–acceptor bond.[93] This is revealed by the linear relationship between the enthalpy of formation of the complex ($-\Delta H_c$) and the extent of charge transfer from the donor to the acceptor. For the complexes of aluminium and gallium compounds with aliphatic *n*-donors, the relationship has the form:[147]

$$-\Delta H_c \text{ kcal mole}^{-1} = 69.2\,\mu_{DA}/er_{DA} - 1.6 \qquad (1)$$

For the complexes with carboxylic acids, a similar relationship is observed:[148]

$$-\Delta H_c \text{ kcal mole}^{-1} = 38.0\,\mu_{DA}/er_{DA} + 3.9 \qquad (2)$$

According to Eqns.(1) and (2), complexes with identical degrees of charge transfer should have identical enthalpies of formation. The values of $-\Delta H_c$ for complexes of aromatic and corresponding aliphatic *n*-donors with the same acceptor should therefore be similar. It can be seen from Table 4, however, that the values of $-\Delta H$ for complexes with aromatic compounds are much lower than those for aliphatic compounds. This has been established for a wide range of complexes of strong acceptors with amines,[93,94,146] ethers, sulphides,[93,146,147,150,151] and phosphines.[19,93,147,149] The observed difference ($\Delta\Delta H$) in the values of $-\Delta H$ are due to the expenditure of energy in the rearrangement of the aromatic *n*-donor on complex formation, that is in the breakdown of $p\pi$-conjugation.

Thus the study of complex formation opens up a route for determining the values of the energy of $p\pi$-conjugation ($E_c$). In the simplest and crudest version, the energy of $p\pi$-conjugation can be estimated as the difference ($\Delta\Delta H$) in the values of $-\Delta H$ for the complexes of a given acceptor with aliphatic and corresponding aromatic donors.[19,88,93,94,146,149,150] The values of $\Delta\Delta H$ for each aromatic donor, obtained by the method of complex formation with different acceptors, agree well with one another, although the acceptors used differ considerably in their strength and in the nature of the interaction; the halides of group III metals[19,93,146] and carboxylic acids[94,149] were studied.

An unsatisfactory feature of this approach is that inductive and steric effects are underestimated. More accurate values of the energy of $p\pi$-conjugation ($E_c$) can be obtained using correlation equations relating the values of $-\Delta H$ to the sum of the induction ($\Sigma\sigma^*$) and steric ($\Sigma E_s^0$) constants of the substituents on the heteroatom of the donor. An equation of this kind has been obtained[147] for complexes of gallium trichloride with a number of aliphatic ethers containing substituents with markedly different induction and steric constants. Using this equation, it is possible to calculate the value of $(-\Delta H)_{calc}$ for an aromatic ether in accordance with the values of $\Sigma\sigma^*$ and $\Sigma E_s^0$, and the energy of $p\pi$-conjugation for the ether can be determined as the difference $E_c = (-\Delta H)_{calc} - (-\Delta H)_{expt}$. This method of determining $E_c$ is independent of the linear relationship (1), and is essentially a second, independent method of determining $E_c$ from data on the heats of formation of the complexes.

In the determination of $E_c$ by this method it is important to estimate correctly the values of $\sigma^*$ and $E_s^0$ for the phenyl substituent. The induction constant of the phenyl substituent is +0.6,[152] but the choice of the steric constant is more complicated. Because of the marked difference in the dimensions of the phenyl group in the plane of the ring and at right angles to it, two steric constants are given for this substituent ($E_s^0 = -0.3$ and $-2.77$ [147,153]). In complexes in which the $p\pi$-conjugation is broken down, the ring occupies the most favourable position from the viewpoint of steric conditions. For example, in the complex $C_6H_5OCH_3.AlBr_3$, the plane of the ring is perpendicular to the COC plane.[150] The low value of the steric constant $E_s^0 = -0.3$ apparently reflects fairly objectively the steric influence of the phenyl substituent in this complex. The same value of $E_s^0$ for the phenyl substituent was used[147] to calculate the energy of the $p\pi$-conjugation of aromatic phosphines. This estimate of $E_s^0$ is confirmed by Tolman's data[74] on the steric effects of phosphine-containing ligands. The steric effects of trimethylphosphine and dimethylphenylphosphine practically coincide, and the steric properties of triphenylphosphine are similar to those of tertiary aliphatic phosphines containing alkyl groups not branched in the α-position.

Since the steric constants of the phenyl substituent and alkyl substituents with the normal structure are similar, steric effects have relatively little influence on the magnitude of $\Delta\Delta H$. The main contribution to the value of $\Delta\Delta H$, in addition to the energy of $p\pi$-conjugation, is made by the difference in the energies of the donor–acceptor bonds due to the difference in the inductive effects of the alkyl and phenyl substituents. This error can be taken into account by introducing into the value of $\Delta\Delta H$ a correction for the inductive effect of the phenyl substituent equal on the average to 1.2 kcal mole$^{-1}$ per ring.[147] The values of $E_c$ for aromatic ethers, sulphides, amines, and phosphines, obtained using the correlation equations, $E_c$(I), and from the values of $\Delta\Delta H$ with a correction for the inductive effect of the aryl fragments, $E_c$(II), are analysed below (see Tables 6 and 7).

The introduction of two *ortho*-substituents leads to the production of appreciable steric hindrance to intermolecular donor–acceptor interaction in $AlBr_3$ complexes. Thus the heat of the addition of $AlBr_3$ molecules to dimethoxydurene (21.2 kcal mole$^{-1}$)[88] is lower than that to aliphatic ethers (23.3 kcal mole$^{-1}$), although the $p\pi$-conjugation in dimethoxydurene is prevented by steric factors (see above). At the same time, in the complexes of aromatic phosphines with trifluoroacetic acid, the influence of *ortho*-substituents on the strength of the donor–acceptor bond is slight, because of the low sensitivity of the H-bond to steric effects. Thus the heats of formation of the complexes $Alk_3P.(CF_3COOH)_2$ in benzene are on the average 27.5 kcal mole$^{-1}$,[149] whereas that for the corresponding complex of diethylmesitylphosphine is 27.3 kcal mole$^{-1}$. Thus the energy of $p\pi$-conjugation in the diethylmesitylphosphine molecule is zero, in agreement with the electronic spectra (see below), which indicate that there is steric inhibition of $p\pi$-conjugation in this compound. The heats of formation of the complexes of trifluoroacetic acid with triphenylphosphine (18.4 kcal mole$^{-1}$) and diethylphenylphosphine (24.6 kcal mol$^{-1}$) are much lower, because of the expenditure of energy in the breakdown of $p\pi$-conjugation on complex formation.

## IV. THE ESTIMATION OF THE DEGREE OF $p\pi$-CONJUGATION

Many physicochemical properties of aromatic compounds of group V and VI elements can be interpreted in terms of the conjugation of the UEP of the heteroatom with the π-electron system of the aromatic fragment. At the present stage of development, some physicochemical methods for studying molecules make possible only comparative estimates of the degree of $p\pi$-conjugation in compounds with similar compositions and structures (UV, NMR, and Raman spectroscopy). Other methods, such as PES, make it possible to characterise quantitatively the degree of $p\pi$-conjugation in certain compounds. The most reliable information on the energy of $p\pi$-conjugation is given by methods involving the measurement of thermal effects such as heats of combustion and the calorimetric study of the electron-donor properties of the corresponding compounds. The results of the study of $p\pi$-conjugated systems by some of these methods can be considered.

### 1. Electronic Spectra

The interaction of the UEP of a heteroatom with a neighbouring π-system can be regarded as an intramolecular donor–acceptor interaction.[1,2] The electronic spectra of aromatic compounds containing a heteroatom should contain intense bands similar in character to the charge-transfer bands of intermolecular charge-transfer complexes. A necessary condition for the appearance of charge-transfer

bands is the overlap of the orbitals of the donor and acceptor in the ground state,[2] or, in the case of aromatic compounds, the overlap of the orbital of the UEP of the heteroatom and the π-system of the aromatic fragment. The conditions of orbital overlap and hence the spectral manifestation of $p\pi$-conjugation are determined to a large extent by the geometry of the molecules.

When there is steric inhibition of the $p\pi$-conjugation in aromatic amines[95] and ethers,[156,157] the spectra of the compounds, in which there is no conjugation, are similar to the spectra of the corresponding aromatic hydrocarbons. For example, in the case of benzoquinuclidine, the orbital of the UEP of the nitrogen atom is orthogonal to the orbitals of the π-system of the aromatic fragment, and the electronic absorption spectrum is similar to that of benzene.[158] The spectrum of dimethoxydurene, in the molecule of which the planes of the methoxy-groups are perpendicular to the plane of the ring (compound (XXVII) in Table 1), is similar to the spectrum of durene.[88] The influence of steric inhibition of $p\pi$-conjugation on the electronic spectra of aromatic sulphides has also been extensively studied,[26,27,157,159,160] but in contrast to the case of amines and ethers, even those aromatic sulphides showing the greatest degree of steric overcrowding absorb more strongly in the near ultraviolet than the corresponding aromatic hydrocarbons.

The nature of the electronic spectra of aromatic phosphines has been discussed for many years (see Refs. 6 and 161–164 and references therein). Recent studies[26,31,165,166] have shown that the electronic spectra of dialkylarylphosphines undergo considerable changes with increase in the volume of the alkyl group or on the introduction of bulky *ortho*-substituents (Table 5). Thus as in the case of aromatic amines, ethers, and sulphides, the nature of the electronic spectra of aromatic phosphines depends on the degree of overlap of the UEP of the phosphorus atom with the orbitals of the π-system, that is on the degree of $p\pi$-conjugation.

Table 5. Parameters of the long-wave band in the ultraviolet spectra of dialkylarylphosphines.

| Phosphine | $\lambda_{max}$, nm | $10^{-3}\varepsilon$ | $10^{3}f$ | Refs. |
|---|---|---|---|---|
| $C_6H_5P(CH_3)_2$ | 251 | 5.6 | 13.0 | [165] |
| $C_6H_5P(C_2H_5)_2$ | 255 | 3.3 | 7.5 | [163] |
| $C_6H_5P(C_4H_9)_2$ | 256 | 3.0 | 7.3 | [163] |
| $C_6H_5P(C_4H_9\text{-iso})_2$ | 257 | 2.4 | 5.9 | [163] |
| $C_6H_5P(C_8H_7\text{-iso})_2$ | 259 | 2.0 | 5.6 | [163] |
| $C_6H_5P(C_4H_9\text{-t})_2$ | 260 | 1.7 | 4.7 | [165] |
| $4\text{-}CH_3C_6H_4P(CH_3)_2$ | 253 | 3.6 | — | [166] |
| $2\text{-}CH_3C_6H_4P(CH_3)_2$ | 254 | 4.8 | — | [166] |
| $2,4,6\text{-}(CH_3)_3C_6H_2P(CH_3)_2$ | 265 | 2.3 | — | [166] |
| $2,4,6\text{-}(CH_3)_3C_6H_2P(C_2H_5)_2$ | 260 | 1.7 | — | [161] |

Symbols: ε is the molar absorptivity, and $f$ the oscillator strength.

The high sensitivity of the electronic spectra to $p\pi$-conjugation makes it possible to detect this effect not only in aromatic sulphides and phosphines but also in the compounds of the elements of later periods,[30,167,168] although the conditions of overlap of the orbital of the UEP with the π-system become less favourable with increase in the atomic number of the heteroatom. For example, it has been shown[30] that as in the case of the compounds of oxygen and sulphur, the intensity of absorption by aromatic compounds of selenium $C_6H_5SeR$ in the near ultraviolet decreases with increase in the volume of the aliphatic group R. The changes in the electronic spectra with change in temperature are characteristic not only of the aromatic sulphides and phosphines,[27,31,168] but also of the triaryl derivatives of arsenic, antimony, and bismuth.[168] This effect is usually attributed to the presence of conjugated and non-conjugated conformers in solution and to the displacement of the conformational equilibrium with change in temperature.

Thus the steric inhibition of $p\pi$-conjugation is clearly revealed in the electronic spectra, and this makes it possible to establish in narrow series of compounds the relationship between the spectral characteristics and the geometry of the molecules. Quantitative estimates of the degree of $p\pi$-conjugation cannot usually be obtained, however, from spectrophotometric data, particularly when the spectra of compounds with different heteroatoms are compared.[169,170]

One of the main reasons for these difficulties is apparently that for a fairly wide range of $p\pi$-conjugated molecules there is no unique dependence of the parameters of the intramolecular charge-transfer bands on the energy of $p\pi$-conjugation. To continue the parallel between $p\pi$-conjugation and intermolecular donor–acceptor interaction, it may be stated that the relationship between the position and intensity of the charge-transfer bands and the thermodynamic parameters of the complexes is extremely complicated.[1,93,171]

In the comparison of the electronic spectra of aromatic compounds of the elements of periods II and III, it is necessary to take into account not only the effect of $p\pi$-conjugation but also the possible contribution of the *d*-orbitals of the sulphur and phosphorus atoms to the MO of aromatic sulphides and phosphines. Although the concept of unoccupied *d*-orbitals has been criticised,[172,173] it is still widely used,[145,174] and provides a simple and natural explanation of the above differences in the spectral behaviour of the compounds of elements of periods II and III when there is steric inhibition of $p\pi$-conjugation.

It should also be noted that the electronic spectra are integral characteristics of the compounds, and result from the superposition of individual bands. Information on the number of bands and their parameters is necessary for a correct assignment of the bands and the correct comparison of experimental data with quantum-chemical calculations. The integral absorption curve can be described by a set of Gaussians.[154,155,175–177] Most frequently, however, the number of bands is estimated from the number of clearly defined maxima, and bands appearing as shoulders are taken into account or ignored arbitrarily. The problem of distinguishing the bands becomes particularly acute for systems in which there is an equilibrium between conjugated and non-conjugated conformers whose electronic spectra differ considerably.

The breakdown of $p\pi$-conjugation is clearly reflected in the nature of the change in the spectrum on going from an aromatic compound containing a heteroatom to a complex with a strong electron acceptor. The spectra of the complexes of aromatic amines and ethers with the halides of group III metals and strong carboxylic acids are similar to the spectra of the corresponding aromatic hydrocarbons.[93,94,146,178,179] Similar changes in the electronic spectra take place when aromatic amines are protonated.[95] Since the groups $OCH_3$, $MX_3$ and $N(CH_3)_2.MX_3$ have strong inductive ($-I$) effects,[150] the inductive effect of the substituent apparently does not influence the parameters of the long-wave band of the aromatic fragment.

The spectra of aromatic sulphides also change considerably when they form complexes with the halides of group III metals, but in contrast to the complexes of amines and ethers, the complexes of aromatic sulphides absorb much more strongly than the corresponding hydrocarbons. Thus the spectrum of the complex $(C_6H_5)_2S.GaCl_3$ is similar to the

spectrum of diphenyl sulphoxide, and not to the spectrum of benzene.[179] A similar picture is observed when aromatic phosphines form complexes with strong electron acceptors[19] or are protonated.[166] The spectra of these systems differ considerably from those of the corresponding hydrocarbons. The spectrum of a solution of triphenylphosphine in trifluoroacetic acid is similar to the spectrum of triphenylphosphine oxide.[19] These facts agree with the view that the 3*d*-orbitals of the phosphorus and sulphur atoms take part in the formation of the MO of aromatic sulphides and phosphines.

The analogous changes taking place in the electronic spectra of aromatic compounds containing a heteroatom when the UEP of the heteroatom forms an intermolecular donor–acceptor bond on the one hand and when bulky substituents are introduced on the other hand leaves no doubt that the intense absorption in the long-wave range of the electronic spectra of these compounds is related to the interaction of the UEP of the heteroatom with the neighbouring π-system, that is to $p\pi$-conjugation. The spectral manifestation of the breakdown of the $p\pi$-conjugation in aromatic compounds containing a heteroatom when complexes are formed has provided a basis for developing a method for estimating the energy of $p\pi$-conjugation.[93,146]

## 2. NMR Spectroscopy

The parameters of the NMR spectra, namely the chemical shifts (δ) and the spin–spin coupling constants (*J*), show a complex dependence on the structural characteristics of molecules and reflect the influence of various factors (inductive, resonance, steric) on the state of individual fragments of the molecules. Nevertheless, in spite of the fact that the parameters of the NMR spectra depend on many factors, they have been widely used to study the effects of $p\pi$-conjugation. Systematic studies of $p\pi$-conjugation by NMR in aromatic and unsaturated compounds of group VI elements have been described in Refs. 26, 31, 180–189 and references therein.

Comprehensive studies of alkyl phenyl ethers[181,185,187] and sulphides[181,186] showed that the most informative parameters for estimating the effects of $p\pi$-conjugation by NMR are those relating to the atom in position 4 of the phenyl ring. This position in the molecule is less influenced than other positions by the inductive and steric effects of the ER group. The values of $\delta(^{13}C_n)$ for compounds of the type $C_6H_5ER$ are (p.p.m.):

| R | O (Ref.187) | S (Ref.186) | Se (Ref.182) | $CH_2$ (Ref.181) |
|---|---|---|---|---|
| $CH_3$ | 120.92 | 125.06 | 125.55 | 125.67 |
| $C_2H_5$ | 120.57 | 125.74 | 126.24 | 125.67 |
| $C_3H_7$ | 120.25 | 125.68 | 126.16 | 125.58 |
| iso-$C_3H_7$ | 120.55 | 126.72 | 126.84 | 125.62 |
| t-$C_4H_9$ | 123.27 | 128.57 | 128.10 | 125.63 |

Since the value of $\delta(^{13}C)$ is directly related to the electron density on the carbon atom, it follows in accordance with the induction constants of the $ECH_3$ groups that a decrease in the shielding of the $C_n$ atom in the compounds studied should be expected, compared with benzene ($\delta(^{13}C)$ = 128.70 p.p.m.) or ethylbenzene ($\delta(^{13}C_n)$ = 125.67 p.p.m.). The increase in the degree of shielding of the $C_n$ atoms of the compounds studied is a consequence of the $p\pi$-conjugation of the UEP of the heteroatoms with the π-system. Comparison of the values of $\delta(^{13}C_n)$ for R = $CH_3$ indicates that the degree of $p\pi$-conjugation decreases in the order $C_6H_5OCH_3 > C_6H_5SCH_3 > C_6H_5SeCH_3$. The nature of the changes in $\delta(^{13}C_n)$ with increase in the size of R reflects the influence of steric effects on $p\pi$-conjugation. The chemical shifts $\delta(^{13}C_n)$ of alkylbenzenes are practically the same for all compounds. For the oxygen compounds there is a sharp decrease in the shielding only for R = $C(CH_3)_3$. For phenyl alkyl sulphides and selenides, the shielding decreases regularly in the order $C_3H_7$ > iso-$C_3H_7$ > t-$C_4H_9$.

The main reason for the observed regularities is the steric inhibition of $p\pi$-conjugation. This is indicated by the good correlation between the values of $\delta(^{13}C_n)$ and the steric constants $E_s^0(CH_2R)$ of the substituents for phenyl alkyl sulphides[181] and phenyl alkyl selenides.[182] Proof that the observed changes in $\delta(^{13}C_n)$ are due to steric factors is provided by the fact that, in contrast to the phenyl derivatives, in compounds of the mesityl series, for example in mesityl alkyl sulphides,[184] the value of $\delta(^{13}C_n)$ remains constant for all R ($CH_3$, $C_2H_5$, iso-$C_3H_7$, t-$C_4H_9$), since in these compounds the $p\pi$-conjugation is prevented by steric factors.

Thus according to the NMR data, the intensity of the $p\pi$-conjugation in alkyl phenyl compounds of group VI elements is determined to a large extent by the conformation of the molecules, which depends on the volume of the alkyl group. This conclusion is confirmed by the results of a study of the chemical shifts of the signal of the proton in position 4 and by the changes in $J(^1H-^1H)$ and $J(^{13}C-^1H)$ for phenyl alkyl ethers and sulphides.[185–187] A similar conclusion that there is steric inhibition of conjugation was reached on the basis of $^{13}C$ and $^1H$ NMR data for the β-atoms of the vinyl group in alkyl vinyl ethers and sulphides.[180,183,190]

The magnitude of the chemical shift of the $^{17}O$ signal is extremely sensitive to the effects of $p\pi$-conjugation in aromatic and unsaturated oxygen-containing compounds. The $^{17}O$ NMR data for these compounds[189] confirmed the conclusions reached from the $^{13}C$ and $^1H$ NMR data. It was shown that the $p\pi$-interaction between the UEP of the oxygen atom and the aromatic (unsaturated) fragment remains approximately the same for R = $CH_3$, $C_2H_5$, and iso-$C_3H_7$, and changes sharply on going to t-$C_4H_9$.

For aromatic compounds of the group V elements, the NMR studies of $p\pi$-conjugation have been less systematic, and the results are less unambiguous. It has been pointed out[191] that it is difficult to interpret the spectral data, since the NMR spectra of these compounds may be influenced by many different factors. From an analysis of the relationship between $\delta[^{13}C(R^{13}CH_3)]$ and $\delta[^{31}P(R^{31}PPh_2)]$ it was concluded that there is only slight overlap of the orbital of the UEP of the phosphorus atom and the π-system of aryl phosphines.[192] In Ref. 193 it was shown that triarylphosphines show a common correlation with alkylphosphines between $\delta(^{31}P)$ and θ (where θ is the valence angle of the phosphorus atom). Assuming that the inductive influence of the substituents on the magnitude of $\delta(^{13}C)$ in the *para*- and *meta*-positions of monosubstituted benzenes are approximately the same, the authors of a number of studies[192,194] took as a measure of the resonance effects the quantity $\Delta\delta = \delta(^{13}C_n) - \delta(^{13}C_m)$. Analysis of the values of $\Delta\delta$ for arylphosphines[192,194–196] led to the conclusion that there is little $p\pi$-conjugation. According to Ref. 192, the value of $\Delta\delta$ is 0.5 p.p.m. for arylphosphines and 12.5 p.p.m. for dimethylaniline. $^{13}C$ NMR data indicating a marked difference in the ability of N and P atoms to undergo $p\pi$-conjugation have been reported.[197]

At the same time, the results of a study of the anisotropy of the chemical shift of the $^{31}P$ NMR signal for trimethyl- and triphenylphosphines in the liquid-crystal phase have been interpreted[198] in terms of the delocalisation of the UEP of the phosphorus atom in triphenylphosphine. The same conclusion was reached from a study of $J(^{31}P-^1H)$ for phenylphosphines.[199] An analysis of the temperature dependence of the difference $\delta(^{31}C_n) - \delta(^{31}C_m)$ for aromatic phosphines $C_6H_5PR_2$ and sulphides $C_6H_5SR$ for R = $CH_3$, $C_2H_5$, iso-$C_3H_7$, and t-$C_4H_9$ indicates[26,31] that in solution there is an equi-

librium between conjugated and non-conjugated conformers; the concentration of the non-conjugated conformer increases in the R order given. In the case of the planar conformation, the maximum contribution of the UEP of the phosphorus atom to the $p\pi$-conjugation with the ring is ~50% of the contribution of the UEP of the nitrogen atom in dimethylaniline.

### 3. Photoelectron Spectroscopy

Photoelectron spectroscopy (PES) is an extremely promising method for studying intramolecular interactions.[200] When combined with quantum-chemical calculations, this method makes it possible to characterise quantitatively the energies of the MO of the molecules and to assign the bands in the PES. The application of this method to organic and heteroorganic compounds has been examined in general reviews[200,201] and also in special reviews on the PES of phosphorus compounds,[202,203] the PES of oxygen and sulphur compounds,[204] and the use of PES to study the conformations of molecules.[205]

The parametrisation of quantum-chemical calculations from PES data is widely used in the study of the regular features of the production of MO. In particular, for aromatic compounds of group VI elements of the type $C_6H_5ECH_3$, the contribution of the UEP of the heteroatom to the HOMO has been determined, and it has been shown that the energy of the HOMO calculated by the simple MO method agrees well with the experimentally determined value.[30,124] The regular features of the influence of the size of the aliphatic group R in series of compounds of the type $C_6H_5ER$ on the conformation of the molecules have been determined.[3,30] It has been shown that in disubstituted benzenes with two electron-donor substituents, the greater contribution to the HOMO is made by the substituent with the lower IP.[206] The conditions for steric inhibition of $p\pi$-conjugation in substituted benzenes have been determined.[207,208] It has been shown for the case of compounds of group VI elements that PES combined with quantum-chemical calculations makes it possible to reach conclusions about the three-dimensional structure of molecules.[209]

A number of papers[202,210-216] have described the geometry and $p\pi$-conjugation of compounds of phosphorus and other group V elements. It has been established that $IP_1$ is linearly dependent on the valence angle of the heteroatom in the phosphine series,[18] and also in more extensive series of compounds of group V elements.[210] In the estimation of the extent of $p\pi$-conjugation in aromatic phosphines, it was first concluded from the interpretation of the PES that there is practically no $p\pi$-conjugation or that it is negligible.[211-213] Later more detailed PES studies and quantum-chemical calculations led to the conclusion that the UEP of the phosphorus atom makes a significant contribution to the HOMO of phenylphosphine and other aromatic phosphines.[164,214,216]

There are a number of different approaches in the use of PES to estimate the extent to which the UEP of the heteroatom is combined with the $\pi$-system. In certain series of compounds, a relative characteristic of the extent of $p\pi$-interaction can be obtained by comparing the values of the resonance integrals $\beta_{E-C}$ calculated from PES data.[217] This parameter has been used to estimate the degree of binding of the UEP in compounds of the type $C_6H_5OR$ and in isologues of anisole,[3,5,218] and in a comparison of the effects of $p\pi$-conjugation in non-substituted and perfluorinated thiophenols, thioanisoles, and diphenyl sulphides.[219]

In accordance with the scheme given in the Figure, the relative efficiency of $p\pi$-interaction has been characterised[219-221] using the difference in the energies of the HOMO ($\pi_1$) and the levels $\pi_2$ or $\pi_3$: $\Delta_{1,2} = \pi_1 - \pi_2$ or $\Delta_{1,3} = \pi_1 - \pi_3$; both quantities can be estimated from the PES. The parameter $\Delta_{1,3}$ can also be obtained from the X-ray fluorescence spectra.[221] The numerical values of $\Delta_{1,2}$ and $\Delta_{1,3}$ have been used to estimate the degree of $p\pi$-interaction and the conformations of the molecules of diphenyl sulphide and other sulphur compounds,[220] aryl alkyl and diaryl sulphides and their perfluorinated analogues,[219,220] and various phosphines.[202]

The PES is influenced considerably, however, not only by $p\pi$-conjugation but also by other factors such as the inductive and steric influence of the substituents, hyperconjugation, $p_\pi$–$d_\pi$ conjugation, etc. Thus the approach described above is useful for comparing the effects of $p\pi$-conjugation in series of compounds with similar compositions and structures.

In addition to PES, X-ray electron spectroscopy (XES) is extremely promising for the analysis of $p\pi$-conjugation. It has been suggested[222] that a measure of the binding of the UEP in a compound being studied is provided by the quantity $\Delta = IP - IP_{stand} - 0.8(E_i - E_{i(stand)})$, where IP and $IP_{stand}$ are the ionisation potentials (determined from the PES), and $E_i$ and $E_{i(stand)}$ are the binding energies of the internal electrons of the heteroatom (determined from the PES) for the compound being studied and a compound taken as standard respectively. A positive value of $\Delta$ corresponds to bonding character for the UEP, and a negative value corresponds to antibonding character. The combined analysis of the ionisation potentials of the outer and inner electrons of the $p\pi$-conjugated molecule being studied and the molecule of the standard compound, in which the UEP of the heteroatom is not combined, makes it possible to eliminate the influence of differences in the charges of the atoms and other electronic effects.

The values of $\Delta$ have been determined for a number of $p\pi$-conjugated molecules. It has been shown that in aliphatic amines, the UEP of the nitrogen atom has antibonding character (for trimethylamine $\Delta = -0.9$ eV), and this has been attributed to the repulsion of the UEP by the electrons of the C–H bonds. On the other hand, for the aniline molecule, $\Delta = 1.3$ eV, indicating that the UEP of the nitrogen atom is combined to a considerable extent with the $\pi$-system. Similarly, the UEP of the oxygen atom of dimethyl ether ($\Delta = -1.8$ eV) is antibonding, whereas in the phenol molecule ($\Delta = 0.7$ eV) it is combined with the $\pi$-system of the ring.

Thus the combined use of PES and XES makes it possible to estimate quantitatively the effects of $p\pi$-conjugation.

### 4. The Energy of $p\pi$-Conjugation from Thermochemical Data

Like any interaction, $p\pi$-conjugation is characterised quantitatively by its energy. At the present time, the energy of $p\pi$-conjugation is determined by two thermochemical methods: a method based on the measurements of heats of combustion, and the recently developed method of complex formation. The first method has been known for a long time, but the data obtained by this method are extremely contradictory;[93,146,173] there have been no systematic studies of aromatic compounds containing a heteroatom, apart from work[223] on the measurement of the heats of combustion of a series of alkyl and aryl vinyl ethers $H_2C{=}CHOR$ and the determination (with a correction for the inductive effect) of the values of the energies of $p\pi$-conjugation $E_c$ (kcal mole$^{-1}$) of the following compounds:

| R | $C_2H_5$ | $C_3H_7$ | iso-$C_3H_7$ | $C_4H_9$ | $C_2H_4Cl$ | $C_6H_5$ | $H_2C{=}CH$ |
|---|---|---|---|---|---|---|---|
| $E_c$ | 6.8 | 6.8 | 6.5 | 7.3 | 7.3 | 6.6 | 10.1 |

In Refs. 223 and 224, the MINDO/2 method gave estimates of $E_c$ agreeing with experimental data. The method of determining $E_c$ from heats of combustion has much in common with the method of complex formation, the principles of which were described above; the values of $E_c$ obtained are given in Tables 6 and 7. Both methods are based on the comparison of the thermochemical properties of aromatic and corresponding aliphatic compounds with allowance (in recent studies) for the differences in the inductive effects of the corresponding groups on the heteroatom.

**Table 6.** Values of the energy of $p\pi$-conjugation (kcal mole$^{-1}$).*

| Compound | $E_c$ (I) | $E_c$ (II) |
|---|---|---|
| $C_6H_5OCH_3$ | 6.2 | 6.2 |
| $C_6H_5OC_2H_5$ | 4.8 | 5.5 |
| $(C_6H_5)_2O$ | 8.8 | 8.6 |
| $C_6H_5SCH_3$ | — | 3.7 |
| $C_6H_5SC_2H_5$ | — | 2.7 |
| $(C_6H_5)_2S$ | — | 5.5 |
| $C_6H_5N(CH_3)_2$ | — | 8.4 |
| $(C_6H_5)_2NCH_3$ | — | 14.6 |
| $C_6H_5P(C_2H_5)_2$ | 5.2 | 3.0 |
| $(C_6H_5)_2PC_2H_5$ | — | 4.9 |
| $(C_6H_5)_3P$ | 7.1 | 6.9 |
| $(4\text{-}CH_3C_6H_4)_3P$ | — | 4.9 |
| $2,4,6\text{-}(CH_3)_3C_6H_2P(C_2H_5)_2$ | — | ~0 |

*The values of $E_c$(I) were obtained using the correlation equations, with the acceptor $GaCl_3$;[147] the values of $E_c$(II) were obtained from the values of $\Delta\Delta H$ [19,94,146,149,150] with a correction for the inductive effect of the aryl ring, the acceptors were metal halides and carboxylic acids, and the average values are given.

**Table 7.** Values of the energy of $p\pi$-conjugation for aromatic ethers (kcal mole$^{-1}$).*

| Compound | $E_c$ (I) | $E_c$ (II) | Compound | $E_c$ (I) | $E_c$ (II) |
|---|---|---|---|---|---|
| $C_6H_5OCH_3$ | 6.2 | 6.2 | $1,4\text{-}(CH_3O)_2C_6(CH_3)_4$ | — | 0 |
| $3\text{-}CH_3C_6H_4OCH_3$ | 5.8 | 5.5 | $C_6H_5OC_2H_5$ | 4.8 | 5.3 |
| $4\text{-}CH_3C_6H_4OCH_3$ | 5.4 | 5.3 | $(C_6H_5)_2O$ | 8.8 | 8.9 |
| $3,5\text{-}(CH_3)_2C_6H_3OCH_3$ | — | 5.3 | $3\text{-}CH_3C_6H_4OC_6H_5$ | — | 8.9 |
| $2,6\text{-}(CH_3)_2C_6H_3OCH_3$ | — | 0.6 | $4\text{-}CH_3C_6H_4OC_6H_5$ | — | 8.9 |
| $3\text{-}BrC_6H_4OCH_3$ | 6.8 | 6.9 | $(4\text{-}CH_3C_6H_4)_2O$ | — | 8.3 |
| $4\text{-}BrC_6H_4OCH_3$ | 6.4 | 6.5 | $(4\text{-}BrC_6H_4OC_6H_5)$ | — | 9.4 |
| $1,2\text{-}(CH_3O)_2C_6H_4$ | — | 9.1 | $(4\text{-}BrC_6H_4)_2O$ | — | 10.5 |
| $1,3\text{-}(CH_3O)_2C_6H_4$ | — | 15.9 | $4\text{-}CH_3OC_6H_4OC_6H_5$ | — | 19.5 |
| $1,4\text{-}(CH_3O)_2C_6H_4$ | — | 12.8 | $4\text{-}CH_3OC_6H_4OC_6H_4Br\text{-}4$ | — | 19.6 |

*The values of $E_c$(I) were obtained by the method of complex formation using correlation equations, with $GaCl_3$ as the acceptor;[147] the values of $E_c$(II) were obtained from the values of $\Delta\Delta H$ [88,90,150,151] with a correction for the inductive effect of the aryl ring, with $AlBr_3$ and $GaCl_3$ as the acceptors.

The values of $E_c$(I) and $E_c$(II) (Tables 6 and 7), obtained by measuring the heats of complex formation by two independent methods (see section III), are similar to one another. The values of $E_c$ for the compounds studied vary over a wide range (0–20 kcal mole$^{-1}$), depending on the nature of the heteroatom and the substituents, the steric conditions, etc. In a series of analogous compounds (Table 6), the heteroatoms can be arranged in the following order of decreasing ability to take part in $p\pi$-conjugation: N > O > S ≅ P. The energy of $p\pi$-conjugation for aromatic amines is approximately three times that for the corresponding phosphines.

The effects of the steric inhibition of $p\pi$-conjugation in aromatic ethers, revealed in the UV, NMR, and PE spectra, are characterised quantitatively by the data in Table 7. The energy of $p\pi$-conjugation for anisole is fairly high (6.2 kcal mole$^{-1}$). The introduction of two $CH_3$ groups in the 2,6-positions of the phenyl ring removes the methoxy-group from the conjugation; $E_c$ for 2,6-dimethylanisole is only 0.6 kcal mole$^{-1}$. The effect of the steric inhibition of $p\pi$-conjugation is revealed by comparing the values of $E_c$ for 1,4-dimethoxybenzene (12.8 kcal mole$^{-1}$) and dimethoxydurene (~0). A similar picture is observed for aromatic phosphines (Table 6). In diethylmesitylphosphine, the $p\pi$-conjugation is destroyed for steric reasons, and accordingly $E_c \cong 0$, whereas $E_c$ for diethylphenylphosphine is 3–5 kcal mole$^{-1}$, and that for triphenylphosphine is ~7 kcal mole$^{-1}$.

The introduction of the electron-donor $CH_3$ group in the 2-, 3-, or 4-position or of two $CH_3$ groups in the 3,5-positions of the phenyl ring of anisole leads to a decrease in the energy of the $p\pi$-conjugation of the UEP of the oxygen atom with the ring. On the other hand, electron-acceptor substituents (the Br atom) lead to an increase in $E_c$ (Table 7).[88,150,151]

An interesting feature is that the introduction of a $CH_3$ group into the 3- or 4-position of one of the rings of diphenyl ether, in contrast to anisole) is not accompanied by a decrease in the energy of $p\pi$-conjugation (Table 7). In these compounds, a conformation ensuring $p\pi$-conjugation of the UEP of the oxygen atom with the $\pi$-system of the non-substituted ring is produced (see above). Electron-acceptor substituents (for example Br) lead to better overlap of the UEP of the oxygen atom with the $\pi$-system of the substituted ring and to less effective overlap with the non-substituted ring. In accordance with this, the value of $E_c$ for $4\text{-}BrC_6H_4OC_6H_5$ is greater than that for diphenyl ether. The question of the energy of $p\pi$-conjugation and the conformation of diphenyl ethers with different substituents ($CH_3$, Br, $OCH_3$, $OC_6H_5$) has been examined.[151]

The values of $E_c$ for *ortho*-, *meta*-, and *para*-dimethoxybenzene, given in Table 2, represent the total energy of conjugation of two methoxy-groups. The energy of the $p\pi$-conjugation of *para*-dimethoxybenzene is slightly less than that of *meta*-dimethoxybenzene, because of the "saturation" effect.[88,152] The energy of conjugation of *ortho*-dimethoxybenzene is even lower,[90] apparently because one of the methoxy-groups is not coplanar with the ring (see above).

Continuing the parallel between $p\pi$-conjugation and intermolecular donor–acceptor interaction, it should be noted that the significance of the value of $E_c$ determined by thermochemical methods corresponds to the enthalpy of formation of the complex ($-\Delta H_c$), which in addition to the energy of the donor–acceptor bond ($-\Delta H_{DA}$) also contains a contribution from the energy of the rearrangement of the molecules of the donor and the acceptor on complex formation. Similarly, the energy of $p\pi$-conjugation ($E_c$), in addition to the energy of the $\pi$-bond between the heteroatom and the $\pi$-system, contains a contribution associated with the differences in the geometries of the aromatic and aliphatic molecules, for example a contribution associated with the difference in the steric interactions.[225] On complex formation with strong electron acceptors, these differences in the geometries, which are most clearly defined in the case of amines, are levelled out. In the determination of the energy of the $p\pi$-conjugation of strained molecules by the method of complex formation, it must be borne in mind that complex formation may

lead to a change in the strain energy, and this will be reflected in the $\Delta\Delta H$ values. This situation has been described[90] for the complexes of cyclic alkylaromatic diethers. The energy of $p\pi$-conjugation of benzo-1,4-dioxan was found to be much too high, since the value of $\Delta\Delta H$ contains a contribution from the change in the strain energy and the conformational rearrangement of the heterocycle.

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The above data indicate fairly reliably that there is intramolecular $p\pi$-interaction not only in aromatic compounds of nitrogen, oxygen, and sulphur, but also in compounds of the heavier elements of groups V and VI, and particularly in phosphorus compounds. The problem of $p\pi$-conjugation in phosphorus compounds has been widely discussed.[6,19,31,161-166,226,227] The use of accurate and sensitive methods will apparently make it possible to find new hetero-organic compounds in which $p\pi$-interaction with an aromatic system may take place.

While the present review was being prepared for publication, new reviews[228,229] and original papers on the geometry of $p\pi$-conjugated molecules[230-233] and the study of $p\pi$-conjugation by electron spectroscopy, NMR, PES, quantum-chemical methods, etc.[234-240] were published.

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# The Reduction of Organic Compounds by Solvated Electrons Generated Electrochemically

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The present review deals with the reduction of organic compounds by solvated electrons generated at a cathode. The general conditions necessary for the electrochemical production of solvated electrons, and the systems in which this process is possible, have been examined. The characteristic features of the reactions of organic compounds with solvated electrons compared with other methods of reduction have been discussed.
Specific data on the reduction by solvated electrons of individual classes of substances difficult to reduce, aromatic and unsaturated compounds, ketones, and derivatives of carboxylic acids—amides, nitriles, and esters—have been examined.
The review will be useful for specialists in the physical chemistry of solvated electrons, theoretical electrochemistry, the electrochemistry of organic compounds, and organic synthesis.
The bibliography contains 92 references.

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## I. INTRODUCTION

Among the varied methods for the electrochemical synthesis of organic compounds, reduction by solvated electrons generated at a cathode has found application in recent years.

Solvated electrons in the liquid phase can be obtained by various methods, chiefly radiation-chemical, photochemical, and photoelectrochemical methods, via atomic or molecular hydrogen, by dissolving alkali metals, and by cathodic generation. Not all of these methods, however, are suitable for the preparative reduction of organic compounds. The most universal method of obtaining solvated electrons is the radiation-chemical method. In systems based on the most varied solvents,[1] solvated electrons are obtained by the removal of electrons from molecules, ions, or atoms by the action of X-rays or gamma-radiation, and also fast electrons. In photochemical generation, solvated electrons are produced by the action of light on substances which are electron donors.

These two methods, however, in addition to solvated electrons, produce radicals and ions which react rapidly with electrons, and this makes it difficult to use these methods of generation for the preparative reduction of organic compounds. Unstable systems are also produced when the electrons are obtained by photoelectrochemical methods.[2]

When a mixture of molecular and atomic hydrogen is passed through aqueous alkali solutions with pH > 12, hydrated electrons ($e_h^-$) are formed:[3-5]

$$H + OH^- \rightarrow e_h^- \ .$$

In liquid ammonia, molecular hydrogen reacts with the amides anion:

$$^1/_2H_2 + NH_2^- \rightleftharpoons e_s^-$$

where $e_s^-$ is the solvated electron. The process takes place at high pressures of hydrogen and high concentrations of potassium amide.[5-8] The reactions with hydrogen have a restricted range of application, however, since they are known only for water and ammonia, and require complex apparatus.

For the reduction of organic compounds by solvated electrons, it is more convenient to use the solution of alkali metals and electrochemical generation. These methods make it possible to produce systems in which the solvated electrons are stable. In many cases, electrolysis makes it possible to control the concentration of electrons and to carry out a process repeatedly. The use of cathodic generation makes it possible to avoid dangerous operations with alkali metals. The main limitations of generation are associated firstly with the use of a conducting medium, that is the use of electrolytes and a solvent with a fairly high dissociating power, and secondly with the need to work in a medium stable to cathodic reduction.

## II. SYSTEMS FOR GENERATING SOLVATED ELECTRONS ELECTROCHEMICALLY

The electrochemical generation of solvated electrons takes place at very negative potentials. Table 1 compares the values of the standard equilibrium potential of the electron electrode with the corresponding values for other electrodes. The term "electron electrode" is used to describe an inert metallic electrode in which the electrons ($e_m^-$) are in equilibrium with solvated electrons in a solution.

**Table 1.** Standard equilibrium potentials ($\phi_0$, V).[9]

| $e_s^- \rightleftharpoons e_m^-$ | $Na \rightleftharpoons Na^+ + e_m^-$ | $K \rightleftharpoons e_m^- + K^+$ | $Rb \rightleftharpoons Rb^+ + e_m^-$ | $Cs \rightleftharpoons Cs^+ + e_m^-$ | $Li \rightleftharpoons Li^+ + e_m^-$ |
|---|---|---|---|---|---|
| Water (n.h.e. in water, 25 °C) | | | | | |
| −2.77—−2.88 | −2.714 | −2.924 | −2.925 | −2.923 | −3.045 |
| Ammonia (n.h.e. in ammonia, 25 °C) | | | | | |
| −1.95 | −1.89 | −2.04 | −2.06 | −2.08 | −2.34 |
| HMPA (s.c.e. in water, 5.5 °C) | | | | | |
| −3.02—−3.05 | −2.92 | −3.04 | −3.00 | −2.96 | −3.21 |

Note: n.h.e. = normal hydrogen electrode; s.c.e. = saturated calomel electrode.

The data in Table 1 show firstly that the potentials of the electron electrode are close to the potentials of the alkali metals, that is the reducing power of solvated electrons is comparable with that of the strongest reducing agents known at present.

In the case of liquid ammonia, the decrease in the difference in the standard potentials of the electron and hydrogen electrodes is due to the higher energy of formation of the ammonium ion from the hydrogen ion, compared with the energy of formation of the hydroxonium ion in water. Secondly, the cathodic generation of electrons can be carried out only in systems in which neither the solvent nor the background salts undergo direct reduction at very negative potentials. In spite of the severity of this requirement, the electrochemical generation of solvated electrons can be carried out in a whole range of systems, which are classified in Table 2.

Table 2. Classification of systems suitable for the cathodic generation of solvated electrons.[10]

| A Solvated electrons stable | | B Solvated electrons unstable | |
|---|---|---|---|
| A-2 | A-2 | B-1 | B-2 |
| Liquid ammonia, HMPA $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$ | methylamine, glyme*, diglyme**, ethylenediamine, $Li^+$, $Rb^+$, $Cs^+$ | HMPA, dimethyl, sulphoxide, diglyme, $NAlk_4^+$ | HMPA–water (alcohol), diglyme–water, $NAlk_4^+$ |

*Glyme = 1,2-dimethoxyethane; **diglyme = dimethyl ether of diethyleneglycol.

The cathodic generation of electrons is most frequently carried out using systems in which the solvated electrons are chemically stable. These are the systems in liquid ammonia, hexamethylphosphortriamide (HMPA), amines, and ethers (group A). The counter-ions in the systems of this group are generally alkali metal cations, although in liquid ammonia at low temperatures it is possible to use salts of aluminium, magnesium, the tetra-substituted ammonium ion, etc. In the systems of sub-group A-1, it is thermodynamically more favourable for the cathodic generation of solvated electrons to take place on solid electrodes, that is for an electron to be removed from the metal into the solution, $e_m^- \rightarrow e_s^-$, and not the deposition of the alkali metal, $M^+ + e_m^- \rightarrow M$. For the same reason, the reaction in the volume involving the reduction of the cations of the background by solvated electrons, $M^+ + e_s^- \rightarrow M$, does not take place. Table 1 shows that for liquid ammonia and HMPA, the standard equilibrium potential of the electron electrode is more positive than the potential of the lithium electrode, and is close to the potentials of the other alkali metals. Under real cathodic generation conditions, dilute ($10^{-5}$–$10^{-2}$ M) solutions of solvated electrons are formed, displacing the equilibrium potential of the electron electrode by 0.1–0.3 V to more positive values. In the case of HMPA, the binding of electrons by the cations of all alkali metals except lithium to form stable non-paramagentic associates $M^+..2e^-$ acts in the same direction.[10] The ratio of the potentials expected from this indicates that generation is thermodynamically preferred to the deposition of the alkali metal.

In the systems of sub-group A-2, the reactions involving reduction are not thermodynamically unfavourable for all alkali metal cations. Electrolytic deposition of the metal generally takes place in sodium salt solutions, and cathodic generation of electrons in solutions of lithium, rubidium, and caesium salts. Systems containing potassium salts occupy an intermediate position.

All the solvents of group A are thermodynamically unstable to the action of high cathodic potentials and solvated electrons. In these systems, however, the reduction of the solvent at the electrode and the chemical reaction of the solvent with solvated electrons in the volume are kinetically hindered (see below).

The systems of group B include solutions of tetra-alkylammonium salts (mainly tetrabutylammonium salts) in aprotic solvents (sub-group B-1) or mixtures of an aprotic and a protonic solvent (sub-group B-2). In these systems there is kinetic retardation of the cathodic reduction of the components of the solution at the electrode, whereas the chemical reaction of the electrochemically generated electrons with some component of the solution takes place relatively rapidly. The electrons disappear by reacting with the cations of the salt or the molecules of the solvent.

It can be seen from Table 2 that the question of the participation of solvated electrons in reduction processes can be raised not only when liquid ammonia and similar solvents are used, but also in systems with an appreciable concentration of proton donors.

Table 3. Physical properties of the solvents.[10]

| Solvent | M.p., °C | B.p., °C | $E$ (T, °C) | $\eta$, cP (T, °C) | DN | AN |
|---|---|---|---|---|---|---|
| Ammonia | −77.7 | −33.4 | 20.0 (−34) | 0.2558 (−34) | 59.0 | — |
| Methylamine | −92.5 | −6.7 | 12.7 (−22.8) | 0.353 (−22.8) | — | — |
| Ethylamine | −81.0 | 16.6 | 5.9 (20) | — | 55.5 | — |
| Ethylenediamine | 11.0 | 116.5 | 12.9 (25) | 1.54 (25) | 55.0 | — |
| Tetrahydrofuran | −65.0 | 64–65 | 7.4 (25) | 0.764 (25) | 20.0 | 8.0 |
| HMPA | 7.2 | 232 | 29.0 (25) | 3.1 (25) | 38.8 | 10.6 |
| Thiohexamethylphosphortriamide | 29.0 | 94 (130 Н/м²) | 39.5 (30) | 5.55 (30) | — | — |
| Glyme | −58.0 | 82–85 | 7.2 (25) | 0.455 (25) | 24.0 | 10.2 |
| Diglyme | — | 161–163 | 7.2 (25) | 2.0 (20) | — | 10.2 |
| Water | 0 | 100 | 78.5 (25) | 1.01 (20) | 18.0 (33) | 54.8 |
| Ethanol | −114.5 | 78.3 | 24.3 — | 1.08 — | — | 37.1 |
| Methanol | −97.5 | 64.5 | 32.6 — | 0.55 — | 19.0 | 41.3 |

Note: $E$ = dielectric constant; $\eta$ = viscosity; DN = donor number; AN = acceptor number.

The suitability of the systems given in Table 2 for the reduction of organic compounds by solvated electrons generated at a cathode is determined chiefly by the ratio of the rates of the reactions of the electrons with the organic compound and with the components of the solution. All the systems of group A are obviously suitable for this purpose. Table 3 gives various physicochemical characteristics of the solvents listed in Table 2. The combination of medium dielectric constant values with high donor numbers ensures that liquid ammonia and HMPA bring about effective dissociation of the background salts and hence effective conductivity of the solution (reaching $10^{-3}$–$10^{-2}$ $\Omega^{-1}cm^{-1}$). Another advantage of liquid ammonia is its ease of purification. The use of this solvent, however, requires increased pressure or reduced temperature. The high boiling point of HMPA makes it possible to use it under ordinary conditions, but the purification of HMPA is very laborious,[11] and the toxicity of this solvent makes it necessary to take special precautions when working with its solutions.[10,12,13]

Of the systems of sub-group B, only the solutions in dimethyl sulphoxide are unsuitable for electrosynthesis using solvated electrons, since dimethyl sulphoxide is an effective acceptor of solvated electrons.[1]

It is important to note that solvated electrons can be generated in mixtures containing considerable quantities of a proton donor, that is essentially in mixed solvents.[14] Solvation in these systems should be heteroselective in character; cations are solvated by the aprotic component, and anions by the protonic component. This ensures the solution and dissociation of the background salts. The solvating power of the protonic component also extends to the solvated electron. Clearly defined heteroselective solvation, for example in mixtures of HMPA with water or alcohol, should lead to an increase in the thermodynamic probability of the cathodic generation of electrons. The strong solvation of cations by HMPA hinders the reduction of the cation of the background salt competing with generation, and strong solvation of the electrons by the protonic solvent ensures the electrochemical generation of electrons.

The cathodic reduction of water and aliphatic alcohols in aprotic solvents is usually difficult, even on platinum. Fig.1 gives the cyclic voltammetric curves in a solution of lithium chloride in mixtures of HMPA and ethanol.[15] The increase in the current strength at higher absolute values of the negative potentials corresponds to the generation of solvated electrons. The peak corresponding to the cathodic reduction of alcohol appears only at a concentration of 50 mole %.

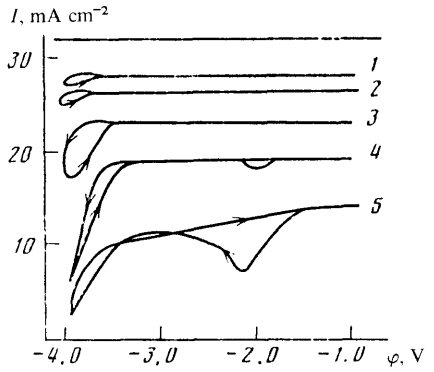



**Figure 1.** Cyclic voltammetric curve (3.3 mV $s^{-1}$) for a platinum electrode in a solution of lithium chloride (0.5 M) in a mixture of HMPA and ethanol; alcohol concentration (mole %): *1*) 0; *2*) 14; *3*) 35; *4*) 50; *5*) 67;[15] (Ag/0.1 M $Ag^+$).

To suppress more reliably the electrode reduction of the protonic component, it is necessary to use metals with a high hydrogen overvoltage (mercury, amalgams), and also to use a tetrabutylammonium salt as background. These salts not only are the most difficult to discharge with the formation of amalgams, but also decrease sharply the rate of the cathodic discharge of water. The retardation can be attributed to the ease of adsorption of the cation on mercury, leading to shielding of the surface, and to a decrease in the concentration of water in the layer next to the electrode as a result of the preferential solvation of the tetrabutylammonium cations by the organic component of the mixed solvent.

Fig.2 gives the cathodic polarisation curves recorded in mixtures of two parts by volume of HMPA with one part by volume of water or ethanol, corresponding to concentrations of the aprotic component of 17 mole % and 42 mole % respectively. According to spectral data,[16] this composition of the mixture with water still ensures the preferential solvation of the electron by water.

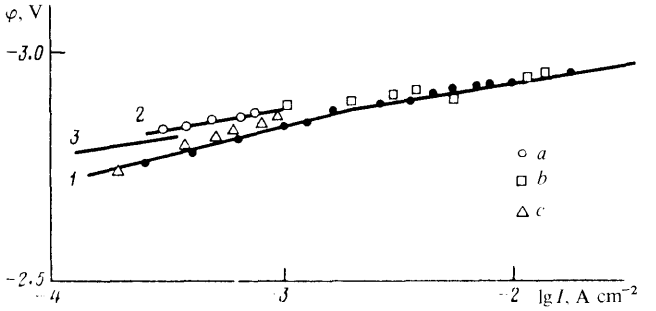



**Figure 2.** Dependence of the potential $\phi$, V (s.c.e.) on the current density ($I$, A $cm^{-2}$) in tetrabutylammonium tetrafluoroborate solutions (0.1 M) at 25 °C; *1*) amalgamated copper (*a*, *b*) in a mixture of HMPA with water (*a*) and with ethanol (*b*), and mercury in a mixture of HMPA with water (*c*); *2*) mercury in hexamethylphosphortriamide; *3*) copper in HMPA.[14]

Curve 1 in Fig.2 shows that the cathodic process in the mixtures takes place at very negative potentials. The potentials in all the systems were measured relative to the saturated calomel electrode in water. The ethanol/water and HMPA/water interphase potential jumps are 30 mV and 150 mV respectively.[17] The interphase potential jumps between water and the systems being studied probably do not exceed 100–150 mV, and this should not introduce qualitative changes in the observed picture. The cathodic process described by curve *1* may correspond to several reactions: the discharge of a proton donor, the discharge of the tetrabutylammonium cation with the formation of an amalgam, and the electrochemical generation of electrons. The first suggestion is not consistent with the similarity in the potentials for the mixtures with water and with alcohol (curves *1a* and *1b*). Moreover, the potentials of curve *2*, recorded in HMPA without water or alcohol, are close to the potentials in mixtures containing a proton donor. Curve *3*, which corresponds to the cathodic process at a copper electrode in HMPA, practically coincides with the curve for a mercury electrode, making it possible to reject the suggestion that the cation is discharged and to assume that the cathodic process is the electrochemical generation of solvated electrons.

The possibility of using protonic media for the reduction of organic compounds by solvated electrons is closely related to the high selectivity of the reactions of solvated electrons. In addition to the reduction of compounds difficult to reduce, solvated electrons liberate hydrogen only very slowly from a whole range of substances containing active hydrogen. It is the low rate of reduction of water and aliphatic alcohols by solvated electrons that makes it possible to use them as proton donors for the reduction of organic compounds. Water in solutions of sodium and lithium perchlorates in HMPA does not

react with solvated electrons up to a water concentration of 0.1 M.[18] Table 4 gives the rate constants for the reactions of solvated electrons with water and alcohols in various media.

Table 4. Rate constants ($k$) for the reactions of solvated electrons with water and alcohols.

| Solvent | Electron acceptor | $k$, litre mole$^{-1}$s$^{-1}$ | Refs. |
|---|---|---|---|
| Water | $H_2O$ | 16 | [1] |
| Ethanol | $C_2H_5OH$ | $4.7 \cdot 10^3$ | [19] |
| Ethylenediamine | $H_2O$ | 24.7 | [20] |
| Heavy water | $D_2O$ | 1.25 | [1] |
| Water | $CH_3OH$ | $\leqslant 1 \cdot 10^3$ | [21] |
| Water | $C_2H_5OH$ | 20 | [21] |

## III. THE REACTIONS OF SOLVATED ELECTRONS WITH THE SOLVENT

The reactions of solvated electrons with organic compounds take place in parallel with their reactions with the molecules of the solvent. All the systems in which solvated electrons are fairly stable are metastable, and gradually decompose as a result of the chemical reaction of the solvated electrons with the solvent. This reaction is generally catalytic, and its rate is increased by impurities, the walls of the apparatus, and reaction products, so that its quantitative study is difficult. There are few published data on this topic. The addition of two electrons to the HMPA molecule gives the dimethylamide anion and the diamidophosphite anion:[22]

$$[(CH_3)_2N]_3PO + 2e_s^- \rightarrow (CH_3)_2N^- + [(CH_3)_2N]_2PO^- \ .$$

In highly purified solutions, it is this reaction that determines the stability of the solvated electrons. The time taken for the disappearance of the colour of a $10^{-2}$ M solution of electrons in a background of sodium perchlorate in HMPA was 4 h at 25 °C and 24 h at 5 °C.[23]

In very pure solutions in liquid ammonia, the reaction is slow, particularly at temperatures of −33 °C and below.

$$NH_3 + e_s^- \rightarrow NH_2^- + {}^1/_2H_2 \ .$$

The rate of the reaction is increased with increase in temperature and under the influence of catalysts. The catalysts include platinum black, iron oxides, the walls of the cell, and the products of the reaction of the electrons with impurities. The reaction of solvated electons with liquid ammonia may be more closely related to the reduction of an organic compound. Thus in the reduction of ethylene oxide in liquid ammonia by solvated electrons obtained by dissolving alkaline earth metals, the amide alkoxide, for example $NH_2CaOC_2H_5$, is formed.[24]

The reduction of tetrahydrofuran by solvated electrons generated at a cathode in HMPA has been studied.[15] The ether is not reduced in the absence of a proton donor. At an ethanol concentration of 50 mole %, tetrahydrofuran is converted into a mixture of n-$C_4H_9OH$, n-$C_4H_9OC_2H_5$, and n-$C_4H_{10}$. In the reduction of ethers with one aromatic group, hydrogenation of the ring takes place first. Thus in a mixture of ethanol (67 mole %) with HMPA in a background of lithium chloride, anisole is reduced to methoxycyclohexane.[25]

The possibility that ethers may be reduced in the presence of impurities which are proton donors must be taken into account when they are used for the cathodic generation of electrons.

## IV. THE CHARACTERISTIC FEATURES OF THE REDUCTION OF ORGANIC SUBSTANCES BY SOLVATED ELECTRONS GENERATED AT A CATHODE

Solvated electrons have exceptionally powerful reducing properties. Their electrochemical generation requires high negative potentials, so that solvated electrons cannot be generated in the presence of substances which are easily reduced. It is therefore appropriate to use solvated electrons to reduce substances whose reduction requires fairly high potentials.

The reduction of organic compounds by solvated electrons generated at a cathode is usually carried out in systems in which the solvated electrons are stable. Substances which dissolve alkali metals to give solvated $M^+$ cations and electrons are used for this purpose:

$$M \underset{}{\overset{\text{solvent}}{\rightleftharpoons}} M^+ + e_s^- \ .$$

Table 5. The solubility of alkali metals and the possibility of the cathodic generation of solvated electrons in various media.[10]

| Solvent | Solubility of alkali metals | Cathodic processes in solutions of salts of the corresponding metals |
|---|---|---|
| Liquid ammonia | all alkali metals readily soluble (more than 10 mole per 1000 g solvent) | cathodic generation of electrons in solutions of all alkali metal salts |
| Methylamine | [Li] = 7.4 M*<br>[Na] = $4 \times 10^{-3}$ M<br>[K] = $10^{-2}$ M<br>Cs—soluble | salts:<br>Li—generation of electrons<br>Na—metal deposition<br>K—generation + deposition<br>Cs—generation of electrons |
| Ethylamine | Li—soluble | Li salts—generation of electrons |
| Glyme | Li, Na, K } insoluble<br>Rb, Cs } soluble | salts:<br>Li, Na, K, Rb, Cs } metal deposition<br>generation of electrons |
| HMPA | all alkali metals readily soluble | $NaClO_4$ + 18-crown-6 in solutions of salts of all alkali metals—cathodic generation of electrons |
| Thiohexamethylphosphortriamide | Na—insoluble | Na salts—metal deposition |

*−23 °C.

The relationship between the solubility of an alkali metal in a given solvent and the thermodynamic possibility of carrying out the cathodic generation of electrons in it is given by Makishima's equation:[26]

$$\varphi^0_{M/M^+} - \varphi^0_{e_s^-} = -\frac{RT}{F} \ln a_{M^+} a_{e_s^-}$$

where $\phi^0_{M/M^+}$ is the standard potential of the alkali metal; $\phi^0_{e_s^-}$ the standard potential of the electron electrode; and $a_{M^+}$ and $a_{e_s^-}$ the corresponding activities in a solution saturated with the alkali metal. Makishima's equation shows that the higher the solubility of the alkali metal, the greater the difference in the standard potentials, that is the more thermodynamically favourable the cathodic generation relative to the electrodeposition of the alkali metal, which is the main reaction competing with the generation of electrons. The quantitative application of the equation is difficult, since usually only the total solubilities of the alkali metals in different media are

known, but it provides a good qualitative explanation of the observed regularities illustrated in Table 5.

Comparison of the data in Tables 3 and 5 shows that there is no correlation between the physical properties of the solvents on the one hand and their ability to dissolve alkali metals and the possibility of electrochemical generation of solvated electrons on the other. Thus for example on going from HMPA to thiohexamethylphosphortriamide (on replacing oxygen by sulphur), the dielectric constant and the dipole moment increase. At the same time, however, the medium loses its ability to dissolve alkali metals and hence the possibility of the electrochemical generation of solvated electrons; this can be related to the decrease in the solvation of the alkali metal ions on going to the thio-derivative. Although the solvating power of the medium both with respect to the cation and with respect to the electron should have a decisive influence on the solution of alkali metals and the cathodic generation of electrons, the main influence is usually shown by the solvation of the cations. Tables 3 and 5 show that liquid ammonia and HMPA, which dissolve alkali metals most readily, have high donor numbers, which are combined with relatively high dielectric constant values. Increase in the energy of solvation of the cations displaces the equilibrium potential of an alkali metal in a solution of its own cations to more negative values, and hence increases the thermodynamic probability of the cathodic generation of solvated electrons. This is facilitated both by the use of solvents with high donor numbers and by binding the cations with special complex-forming reagents, cryptates and crown ethers. Complex formation in this way facilitates generation in systems in which the alkali metal is deposited in the absence of the additive (Table 5).

When an organic substance is added to a system in which cathodic generation of solvated electrons can take place, in the general case the stationary polarisation curves show the formation in this way facilitates generation in systems in which are not too negative, direct reduction of the organic compound at the electrode will take place. Under certain conditions, retardation of this process takes place, displacing the potential sharply towards negative values, due to the start of generation (see Fig. 6 below). The limiting current of the electrode reduction of an organic compound may be a diffusion current (supply of the organic substance) or a passivation current (change in the state of the electrode surface as a result of the formation of tarry products by the organic compounds or films of the hydroxides of the cations of the background salts). At the generation potentials, the additive is reduced by two parallel routes: directly at the electrode at a rate corresponding to the limiting current, and as a result of chemical reaction with the solvated electrons. The rate of the direct reduction in the generation range is independent of the potential. With increase in the generation current, the proportion of direct reduction decreases. For many organic compounds, the electrode reduction is hindered for kinetic reasons, and most of the substance is reduced by reaction with solvated electrons.

One of the advantages of the reduction of organic compounds by electrons obtained electrochemically is the possibility of using higher current densities than in direct cathodic reduction. This is due firstly to the high value of the diffusion coefficient of solvated electrons. The corresponding values for water, ammonia, and HMPA are given in Table 6. Solvated electrons are several times more mobile than common ions (the mechanism of the motion is similar to Grotthus' relay mobility). It should be noted that the Walden product (the product of the diffusion coefficient and the viscosity of the solvent) is approximately the same for the three solvents. This feature can be used to estimate the values for solvents with unknown solvated electron mobilities.

A second feature ensuring the rapid removal of solvated electrons from the electrode is intensive convection due to the decrease in the density of the solution at the cathode surface. This phenomenon is related to the increase in the volume of the solution when electrons are introduced into it. In contrast to the electrostriction accompanying the solvation of ordinary ions, the formation of solvated electrons gives an increase in volume of 65–95 ml mole$^{-1}$ for liquid ammonia[5] and ~80 ml mole$^{-1}$ for HMPA.[32] The current densities of the generation of solvated electrons may be 2500 or more time the diffusion currents of organic compounds to the electrode, as demonstrated[33] for the reduction of anthracene.

Table 6. Diffusion coefficients ($D$, cm$^2$s$^{-1}$) of solvated electrons in liquid ammonia, water, and HMPA.

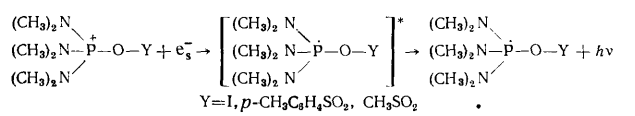
| Solvent | $T$, °C | Method of determination | $10^4 D$, cm$^2$s$^{-1}$ | $10^5 D.\eta$, cm$^2$cP s$^{-1}$ | $D/D_{Na^+}$ | Refs. |
|---|---|---|---|---|---|---|
| Liquid ammonia | —36.0 | chronopotentiometric anodic oxidation of electrons | 1.45 | — | — | [27] |
| | | measurement of electrical conductivity and transport numbers | 1.74 | 4.45 | 6.7 | [28,29] |
| Water | room temp. | radiation-chemical method, measurement of electrical conductivity | 0.49 | 4.90 | 3.7 | [21] |
| Hexamethylphosphortriamide | room temp. | radiation-chemical method, current relaxation curves | 0.14 | 4.59 | 10.0 | [30,31] |

A characteristic feature of the reaction of solvated electrons with organic substances is chemiluminescence. The luminescence is produced simultaneously with the cathodic generation of the solvated electrons, and may be very intense.

One group of reactions accompanied by chemiluminescence consists of the reactions of solvated electrons with organic cations and radical-cations to give neutral molecules or radicals.

Thus cyclic voltammetry with simultaneous recording of the luminescence spectra showed that N,N,N′,N′-tetramethyl-*para*-phenylenediamine does not undergo direct cathodic reduction in a solution of sodium perchlorate in HMPA, but can be oxidised reversibly to a radical-cation which reacts with solvated electrons to give an excited molecule of N,N,N′,N′-tetramethyl-*para*-phenylenediamine, which returns to the ground state with the emission of a quantum of light.[34,35] Similar results were obtained[36] with N,N,N′,N′-tetramethylbenzidine, N,N-dimethylanisidine, and other amine derivatives which form stable radical-cations.

Luminescence was also observed[37] when thoroughly purified solutions of salts of various alkali metals in HMPA were electrolysed under galvanostatic pulse conditions without separating the cathode and anode compartments. It was suggested that the chemiluminescence is due to the reaction of the solvated electrons with a pseudo-phosphonium cation, which gives a neutral radical in an excited state; this radical returns to the ground state with the emission of a quantum of light:




The iodine derivative was formed by the reaction between the solvent and elemental iodine liberated at the anode in potassium iodide solution, and the other two compounds were obtained

by adding tosyl chloride and mesyl chloride respectively to the solution.

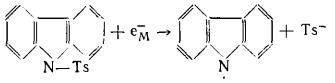
The second group of processes accompanied by the emission of light consists of the reduction of neutral molecules with the simultaneous dissociation of the original molecule. In these processes the formation of the excited state often takes place at the stage of the addition of the second electron, after the dissociative one-electron reduction:[36]

$$(C_6H_5)_3CCl + e_s^- \rightarrow (C_6H_5)_3C^{\cdot} + Cl^- \qquad (C_6H_5)_3C^{\cdot} + e_s^- \rightarrow (C_6H_5)_3C^{-}$$

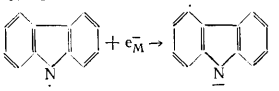
Reactions of this type include the reduction of N-toluenesulphonylcarbazole, examined below, and the reduction of benzyl chloride and diphenylmethyl chloride.[35]

It is of interest to compare the direct cathodic reduction with the reduction of the same substance by solvated electrons. Thus the pseudo-phosphonium cations formed in solutions of iodine, tosyl chloride, and mesyl chloride in HMPA are reduced at potentials more than 2.5 V more positive than the potential of the generation of solvated electrons; this gives non-excited species.[37]

Similarly, N-tosylcarbazole is reduced at an electrode without luminescence at a potential which is 0.8 V more positive than the generation potential of solvated electrons:

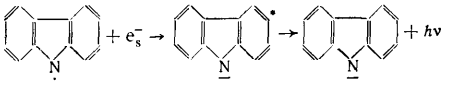



(1)




(2)

As always, chemiluminescence appears when the generation potential of the solvated electrons is reached. It is due to the reaction




The process takes place similarly when HMPA is replaced by a mixture of ammonia and tetrahydrofuran in the volume ratio 2:1.[38]

This system is similar to that in pure ammonia. Tetrahydrofuran ensures the solution of the organic compounds. The reduction of α- and β-naphthol tosylates by solvated electrons in a mixture of ammonia and tetrahydrofuran leads to the emission of light:[38,39]

$$Naph{-}Ts + e_s^- \rightarrow Naph{-}Ts^{\cdot-} \rightarrow Naph^{\cdot} + Ts^-$$
$$Naph^{\cdot} + e_s^- \rightarrow Naph^-$$

Chemiluminescence was also observed when solvated electrons were generated in a solution of sodium perchlorate in HMPA containing 9-chlorofluorene derivatives.[34]

Thus the study of chemiluminescence provides a useful method of studying the mechanism of the reduction of compounds by solvated electrons.

## V. THE REDUCTION OF INDIVIDUAL CLASSES OF ORGANIC SUBSTANCES BY SOLVATED ELECTRONS

From the preparative viewpoint, the use of the electrochemical generation of solvated electrons is most effective for reducing substances which require high negative potentials for electron transfer or which are not reduced at all electrochemically. These compounds are aromatic hydrocarbons, alkenes, aliphatic ketones, amides. and nitriles.

### 1. Aromatic Compounds

The aromatic compound most difficult to reduce is benzene. It is polarographically inactive,[40] and does not undergo direct electrochemical reduction. Direct cathodic reduction of benzene does not take place in liquid ammonia in a background of potassium or methyltributylammonium iodide at silver or gold electrodes.[41]

Benzene does not react with solvated electrons obtained by dissolving alkali metals in liquid ammonia.[1] In the presence of proton donors, however, benzene ir hydrogenated under the influence of solvated electrons. Table 7 gives data obtained by different authors on the preparative electrochemical reduction of this compound, and shows that in some cases the process can be carried out fairly selectively and with a good current efficiency. Allowance must be made, however, for the fact that the data in Table 7 were generally obtained with incomplete transformation of the starting material. The high current efficiencies show that the proportion of side reactions is small. This agrees with the results of Schindewolf and Neumann,[49] which showed that solvated electrons obtained by laser photolysis in a mixture of ammonia and water (25 °C) containing benzene hydrogenate benzene and do not react with the components of the solvent (ammonia and water).

Table 7. Reduction of benzene in aprotic media.

| No. | Solvent | Background | Proton donor | $I$, A cm$^{-2}$ electrode | $T$, °C | Reduction | | Refs. |
|---|---|---|---|---|---|---|---|---|
| | | | | | | product (%) | overall current efficiency, % | |
| 1 | Liquid ammonia | NaCl | ethanol 1-4% | $2 \times 10^{-2}$ platinum | —33 | cyclohexa-1,4-diene (98) | 41* | [42] |
| 2 | HMPA | LiCl | methanol | platinum | — | cyclohexa-1,4-diene (53)<br>cyclohexa-1,3-diene (2)<br>hexene (21)<br>hexane (24) | — | [43] |
| 3 | Ditto | ditto | ethanol 67 mole % | $9.0 \times 10^{-2}$ aluminium | — | cyclohexadiene (23)<br>cyclohexene (10)<br>cyclohexane (67) | 95<br>—<br>— | [44] |
| 4 | Ditto | $LiClO_4$ 0.2 M | water 0.1 M | | — | cyclohexa-1,3-diene | — | [18] |
| 5 | Methyl-amine | LiCl | solvent | $10^{-1}$ platinum | —70 | cyclohexene (100)<br>cyclohexa-1,4-diene (95)<br>cyclohexene (4) | 49[2*]<br>49[3*]<br>— | [45,46] |
| 6 | Ethylene-diamine | LiCl 0.3M | ditto | $2 \times 10^{-2}$ platinum | +25—27 | cyclohexadiene (17)<br>cyclohexene (70)<br>cyclohexane (13) | 64<br>70 | [47][2*] |
| 7 | Ditto | LiCl, 0.3 M | | $7 \times 10^{-2}$ carbon | 33 | cyclohexa-1,4-diene (38)<br>cyclohexane (14.4) | 52,4<br>— | [48][3*] |

Note. 1*) excess of benzene; 2*) diaphragm; 3*) without diaphragm, excess of benzene; 4*) diaphragm, excess of benzene.

The data in Table 7 illustrate the reduction of benzene in media typical of the electrochemical generation of solvated electrons. The addition of proton donors, however, may lead to appreciable reduction of benzene in mixtures of water

with aprotic solvents such as diglyme and sulpholane (Table 8). In these solvents also, the reduction apparently involves the formation of solvated electrons. Thus for example in a diglyme–water mixture the process takes place at a potential of −3.3 V (s.c.e.), which is sufficient for the generation of solvated electrons, and the potential is the same in the presence and in the absence of benzene.

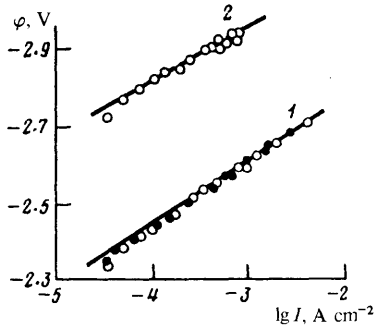



**Figure 3.** Dependence of the potential $\phi$, V (s.c.e.) on the current density at a dropping mercury electrode in aqueous solutions ($c$ = 0.1 M) at 20 °C; *1*) in solutions of tetramethylammonium hydroxide and iodide; *2*) in a solution of tetrabutylammonium hydroxide.[58]

The increase in the proportion of products with a high degree of hydrogenation with increase in the concentration of proton donors is noteworthy (Table 9).

**Table 9.** Reduction of benzene in HMPA–ethanol mixture.[44]

| Cathode | Donor, mole % | $T$, °C | $I$, A cm$^{-2}$ | Reduction product, % | | |
|---|---|---|---|---|---|---|
| | | | | cyclohexadiene | cyclohexene | cyclohexane |
| Al | 66.6 | 28 | $9.1\cdot10^{-2}$ | 20.2 | 8.5 | 71.3 |
| Al | 5 | 28 | $9.1\cdot10^{-2}$ | 81.2 | 16.4 | 2.3 |
| Al | 66.6 | 28 | $3.6\cdot10^{-3}$ | 53.1 | 10.1 | 36.8 |
| Al | 66.6 | −2 | $3.6\cdot10^{-3}$ | 93.0 | 5.8 | 1.2 |
| Pt | 5 | 28 | $9.1\cdot10^{-2}$ | 85.7 | 12.9 | 1.4 |

The favourable influence of a high concentration of proton donors on reductive hydrogenation is also observed in other cases. For example, aromatic sulphides and ethers are also reduced with the participation of solvated electrons generated at a cathode.[15] The cyclic voltammetric curves at a platinum electrode in solutions of lithium chloride in HMPA and its mixtures with ethanol (up to 50 mole %) in the presence of diphenyl sulphide coincided with the curves obtained without adding the organic substance. Table 10 gives the composition of the reduction products for different concentrations of alcohol in the solution, and shows that solvated electrons break the bond between sulphur and the carbon atom of the aromatic ring, with subsequent addition of a proton. In the absence of alcohol, the main reduction product is benzene,

**Table 8.** Reduction of benzene in protonic media.

| No. | Solvent | Background | Electrode | $T$, °C | Reduction | | | Notes | Refs. |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | product | % | overall current efficiency, % | | |
| 1 | Water, diglyme | $(C_4H_9)_4NBr$ (12 g in 80 ml solution) | mercury* | 25—30 | cyclohexa-1,4-diene<br>cyclohexene | 96.3<br>3.7 | 71<br>— | diaphragm, excess of benzene | [50] |
| 2 | Water[2*] 10 ml, ethylenediamine 40 ml | $NH_4Cl$, 2 g<br>$(C_6H_{13})_4NBr$ 0.75[4*] | graphite | — | cyclohexa-1,4-diene<br>cyclohexane | 50<br>2 | 52<br>— | | |
| 3 | Water[3*] 35.8[4*]<br>sulpholane[5*] 52[4*] | $(C_4H_9)_4NBr$ 3.7[4*] | mercury | 40 | cyclohexa-1,4-diene | 98.5 | 70.7 | diaphragm, degree of transformation of benzene 32.8%, homogeneous catholyte | [52] |
| 4 | Diethyleneglycol 87.6[4*] | $(C_4H_9)_4NBr$ 3.7[4*] | mercury | — | cyclohexa-1,4-diene | 91.1 | 68.1 | diaphragm, degree of transformation of benzene 36%, homogeneous catholyte | [53] |
| 5 | Isobutyl[4*] alcohol 87.6 | $(C_4H_9)_4NBr$ 3.7[4*] | mercury | 40 | cyclohexa-1,4-diene | 91.2 | 48.9 | diaphragm, degree of transformation of benzene 31.8%, homogeneous catholyte | [54] |
| 6 | Water | $[(C_4H_9)_4N]_2SO_4$<br>$(C_4H_9)_4NOH$[6*] | mercury | 65 | cyclohexa-1,4-diene<br>cyclohexene | 87<br>13 | 77<br>— | cation-exchange membrane, excess of benzene, heterogeneous catholyte[6*] with stirring | [55] |
| 7 | Water | $(C_4H_9)_4NOH$[7*], pH>11[8*] | mercury | — | cyclohexa-1,4-diene | | 50[9*] | without diaphragm, continuous supply of benzene and removal of product | [56,57] |

* Electrolysis at a controlled potential of −3.3 V (s.c.e.); the potential is the same in the presence and in the absence of benzene.

[2*] Or other amine containing 1–8 carbon atoms.

[3*] Or a lower aliphatic (alicyclic) alcohol.

[4*] Mole %.

[5*] Or sulphoxide.

[6*] $\{(C_4H_9)_4N\}_2SO_4 : (C_4H_9)_4NOH : H_2O : C_6H_6 = 20 : 1 : 71 : 8$ (by weight).

[7*] Can be replaced by $(C_4H_9)_3C_2H_5NOH$ or $(C_3H_7)_4NOH$.

[8*] At high pH values there is a decrease in the liberation of hydrogen and an increase in the stability of the steel anode.

[9*] In a background of $(C_4H_9)_3CH_3NOH$ the yield decreases, and in a background of $(C_2H_5)_4NOH$ and $(CH_3)_4NOH$ reduction does not take place.

for the reduction of which the protons of impurities are sufficient. Without alcohol, benzene is stable to the action of solvated electrons, but in the presence of alcohol, benzene undergoes reductive hydrogenation, which is greater, the higher the concentration of alcohol in the solution.

**Table 10.** The reduction of diphenyl sulphide in solutions of lithium chloride (0.5 M) in mixtures of HMPA and ethanol, 15 °C.[15]

| Alcohol, mole % | Yield of products, % | | | | | | Transformation, % | Current efficiency, % |
|---|---|---|---|---|---|---|---|---|
| | benzene | cyclohexa-1,4-diene | cyclohexa-1,3-diene | cyclohexene | biphenyl | other substances | | |
| 50 | 32.7 | 10.3 | 1.6 | 1.3 | traces | 0.8 | 46.4 | 67.2 |
| 35 | 42.1 | 8.2 | 1.1 | 1.3 | traces | 3.2 | 54.3 | 69.6 |
| 14 | 65.1 | 0 | 0 | 0 | 1.8 | 0 | 66.9 | 61.4 |
| 0 | 84.8 | 0 | 0 | 0 | 1.8 | 2.4 | 88.9 | 79.4 |

An interesting feature is that benzene can be reduced not only in a mixture of an aprotic and a protonic solvent but also in purely protonic media. Thus dihydric and monohydric alcohols, and also water, have proved suitable for this purpose (Table 8).

In aqueous tetrabutylammonium hydroxide solution, the potential of a mercury cathode is displaced to between − 2.5 V and −2.8 V (Fig.3),[58] which is sufficient for the generation of solvated electrons (see Table 1). Tetrabutylammonium cations are adsorbed on the electrode surface, displacing water molecules and hindering their discharge at the electrode.

When purely aqueous solutions are used, a complication not encountered in organic systems arises, due to the low solubility of benzene and many other organic compounds in water (20 °C, M):[59–61]

| | |
|---|---|
| Benzene | $2\cdot10^{-2}$; $2.4\cdot10^{-2}$ (25°C) |
| Toluene | $6\cdot10^{-3}$ |
| *o*-, *m*-, and *p*-Xylenes | $1.6—1.8\cdot10^{-3}$ |
| Phenol | $9\cdot10^{-1}$ |
| α-Naphthol | $3\cdot10^{-4}$ |

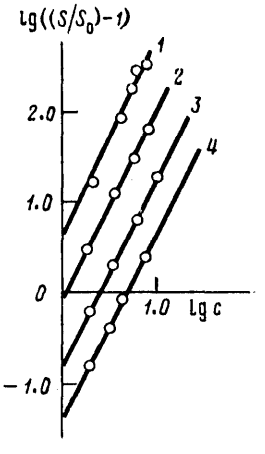



**Figure 4.** Solubility of benzene at 25 °C in solutions of the bromides: *1*) tetrabutylammonium; *2*) tetrapropylammonium; *3*) tetraethylammonium; *4*) tetramethylammonium; *S* is the solubility in the solution; $S_0$ is the solubility in water.[60]

The solubility decreases in the order benzene–toluene–ethylbenzene–mesitylene (1.6–0.6–0.2–0.05 g litre$^{-1}$).[60]

It should be noted, however, that in the presence of tetraalkylammonium cations the solubility of organic compounds increases[61–64] (the "salting-in" effect). The solubility is higher, the higher the concentration of the salt and the longer its alkyl group (Fig.4),[60,61] and also on going from chlorides to bromides and iodides.[64]

The reduction of benzene can also be carried out in a heterogeneous system (emulsion) with vigorous stirring (Table 8). The movement of benzene to the electrode is apparently facilitated by the presence on the elrctrode surface of the electrical double layer of tetrabutylammonium cations, which should help to bring benzene on to the electrode surface.

An examination of different mechanisms of mass transfer and charge transfer in the electrolysis of an emulsion (organic substance–water) showed that an important positive role is played by the hydrophobic tetra-alkylammonium cations.[59]

The behaviour of toluene is analogous to that of benzene. Toluene is also polarographically inert, and does not react with solvated electrons obtained by dissolving alkali metals in liquid ammonia,[1] but it can be reduced by solvated electrons in aprotic, mixed, and protonic media (see Table 11).

**Table 11.** The reduction of toluene.

| Solvent | Background | Proton donor | Electrode | Product (%) | Refs. |
|---|---|---|---|---|---|
| HMPA | $LiClO_4$ $NaClO_4$ | $H_2O \leqslant 0.1$ M | Pt | 1-methylcyclohexa-1,4-diene | [18] |
| HMPA | LiCl | $C_2H_5OH$ 67 mole % | Al | methylcyclohexane (45.4) | [25] |
| Methylamine | LiCl | solvent | Pt | methylcyclohexadiene (94)[1*] | [45[1*], 46[2*]] |
| Ditto | LiCl | ditto | Pt | methylcyclohexene (5)[1*] methylcyclohexane (86)[2*] toluene (14)[2*] | |
| Diglyme–water | $(C_4H_9)_4NBr$ | $H_2O$ | Hg[3*] | 1-methylcyclohexa-1,4-diene (95) | [50][4*] |
| Diethylene glycol | $(C_4H_9)_4NBr$ | solvent | Hg | 1-methylcyclohexa-1,4-diene | [53] |
| Isobutyl alcohol | $(C_4H_9)_4NBr$ | ditto | Hg | 1-methylcyclohexa-1,4-diene | [54] |
| Water | $(C_4H_9)_4NOH$ | » | Hg | reduction | [56] |

Note. 1*) without diaphragm, current efficiency 64%; 2*) with diaphragm, current efficiency 44%; 3*) electrolysis at a potential of −3.3 V (s.c.e.), which is the same in the presence and in the absence of toluene; 4*) current efficiency 61%.

As in the case of benzene, it is possible to select conditions under which the process is fairly selective. The maximum degree of reduction is obtained in a mixed solvent at a high concentration of the protonic component (Table 11).

Table 12 compares the results of the reduction of other aromatic compounds: naphthalene, tetralin (tetrahydronaphthalene), anthracene, and dihydroanthracene, in media in which the cathodic generation of electrons is possible. Like benzene and toluene, tetralin is not reduced at an electrode, for example at mercury in ethylenediamine,[48] but is effectively hydrogenated with the participation of solvated electrons (Tables 12 and 13).

Unlike benzene, toluene, and tetralin, naphthalene and anthracene can be reduced directly at an electrode. Thus in anhydrous ethylenediamine, naphthalene is active at mercury and platinum electrodes.[47,48] The product of the reduction of naphthalene in protonic media is 1,4-dihydronaphthalene.[67] For example, the preparative direct electrode

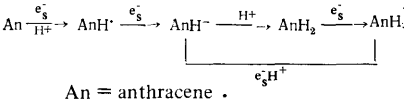
reduction of naphthalene in a mixtpre of acetonitrile and water gives 98% 1,4-dihydronaphthalene mixed with small quantities of 1,2-dihydronaphthalene and tetralin with an overall current efficiency of 86%.[68]

Table 12. The reduction of naphthalene, anthracene, and their derivatives by electrolysis in HMPA and ethylenediamine.

| Medium | Proton donor | Electrode | $I$, A cm$^{-2}$ | Substance | Reduction products (%) | Current efficiency, % | $E_{1/2}$* | Refs. |
|---|---|---|---|---|---|---|---|---|
| LiCl (HMPA) | $C_2H_5OH$ 67 mole % (33 vol.%) | aluminium | $9.1\cdot10^{-2}$ ($-2.4\pm0.1$)2* | naphthalene | dihydronaphthalene (7) tetralin (22) hexalin (20) octalin (11) decalin (40) | 96 | −2.5 | [44]3* |
| LiCl (HMPA) | $C_2H_5OH$4* 67 mole % (33 vol.%) | aluminium | −2.4 V2* | tetralin | hexalin (10) octalin (5) decalin (85) | 54 | — | [65]5*, 6* |
| LiCl, $(C_4H_9)_4NI$ (ethylenediamine) | solvent | platinum graphite carbon | | tetralin7* | hexalin octalin | — | — | [48]8* |
| LiCl (HMPA) | $CH_3COOH$ 1 M | lead | $2\cdot10^{-3}$9* | anthracene | dihydroanthracene (100) | 65 | −2.0 | [66] |
| LiCl (HMPA) | $CH_3COOH$ 1 M | glass-carbon | $5\cdot10^{-3}$ | | di- (2), tetra- (3), hexa- (88), and octa-anthracene10* | 57 | — | |
| | | | $1.3\cdot10^{-1}$ | | tetra- (15) and hexa-anthracene (85) | 53 | — | |
| LiCl (HMPA) | $CH_3COOH$ 1M | aluminium | $1.5\cdot10^{-1}$ | dihydroanthracene | tetra- (70) and hexa-anthracene (30) | — | — | [66] |

Note: *) half-wave potentials (s.c.e.) for the reduction of the substances in a mixture of 75% dioxan + 25% water in a background of tetraethylammonium or tetrabutylammonium iodide;[40] 2*) potential relative to a silver wire in the same solution, which is the same for benzene, naphthalene, and tetralin; 3*) with a diaphragm; 4*) there is practically no reduction in the absence of a proton donor; 5*) polarographically inactive; 6*) with diaphragm; 7*) see Table 13; 8*) without diaphragm; 9*) generation of electrons does not take place at this current density; 10*) traces of the last compound.

In a solution of lithium chloride in HMPA, anthracene gives two cathodic peaks: a peak due to the reversible formation of a radical-anion (+1.23 V)† and a peak due to the irreversible formation of the dianion (+0.33 V)#.[66] As a proton donor is added, a second peak gradually appears beside the first, that is as in the case of naphthalene, hydrogenation of one bond takes place. Tables 12 and 13 show that more extensive hydrogenation takes place under the influence of solvated electrons. Analysis of the preparative electrolysis data shows that, irrespective of the electrode material, the reduction gives a mixture of dihydro-, tetrahydro-, and hexahydroanthracenes. The change in the concentration of these products as electrolysis proceeds (see Fig.5) shows that the reduction takes place in stages, and a more detailed study of the kinetics of the process indicates that the formation of tetrahydroanthracene takes place partly without the stage of dihydroanthracene formation:




An = anthracene .

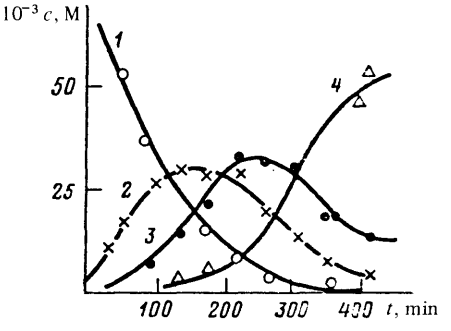



Figure 5. Change in the concentration of anthracene ($c$) and its reduction products at a current density of $1.25 \times 10^{-1}$ A cm$^{-2}$; initial anthracene concentration 0.070 M; *1*) anthracene; *2*) dihydroanthracene; *3*) tetrahydroanthracene; *4*) hexahydroanthracene.[66]

Table 13. Reduction of tetralin by electrolysis in ethylenediamine.[48]

| Background | $T$, °C | Electrode* | Current efficiency, %2* | Products3* | |
|---|---|---|---|---|---|
| | | | | hexalin | octalin |
| Lithium chloride | 33.0 | platinum | 57.9 | 41.6 | 7.5 |
| | | graphite | 70.5 | 55.4 | 11.6 |
| | | carbon | 80.3 | 67.3 | 9.5 |
| Tetrabutylammonium iodide | 28.0 | ditto | 17.0 | 13.0 | 1.8 |
| Ammonium chloride | 20.0 | ditto | 0 | 0 | 0 |

Note: *) current density $7 \times 10^{-2}$ A cm$^{-2}$; 2*) a small fraction of the current is used for the reduction of dihydronaphthalene (impurity in tetralin); 3*) fraction of the current.

Interesting data were obtained[69] on the reduction of naphthalene on platinum in mixtures of alcohols (methanol, ethanol, propan-1-ol, and propan-2-ol) with HMPA in a background of lithium chloride at a high concentration of the protonic component. Naphthalene is not reduced in pure ethanol§. When 10–50 vol.% HMPA is added at a potential which is 1 V more negative than the potential of the electrode reduction of naphthalene, the latter is converted into a mixture of dihydronaphthalene, tetralin, hexalin, and decalin. The value of

†The potentials are given relative to a lithium reference electrode; on this scale, the potential at which the generation of electrons starts is +0.16 V.

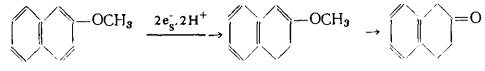
#The direct reduction of anthracene can also be carried out in ethylenediamine.[47]

§ Tetralin also could not be reduced in ethanol containing lithium chloride.[65]

the potential and the nature of the products indicate that the reaction involves solvated electrons, in spite of the high concentration (up to 90 vol.%) of alcohol in the solution.

The example of aromatic compounds illustrates a characteristic feature of reduction by solvated electrons: the rate of the process is independent of the nature of the organic substance. Thus in HMPA, the reduction potentials of benzene, naphthalene, and tetralin coincide.[65] There are very few published data on the reduction of an aromatic ring in compounds containing functional groups. In the HMPA–ethanol system at an aluminium cathode, phenol and anisole are reduced to cyclohexanol and methoxycyclohexane respectively in yields of 51.7% and 45.8%.[25]

2-Naphthyl ethers are reduced selectively to dihydro-compounds, whose hydrolysis gives tetralones which are the starting materials for the synthesis of medicinal products.



This process has been carried out on a large scale.[70]

## 2. Unsaturated Compounds

Table 14 gives data on the reduction of alkenes in systems in which the cathodic generation of electrons is possible. It cannot be concluded, however, that the reaction involves the formation of solvated electrons in all cases. In solutions of lithium chloride and tetrabutylammonium tetrafluoroborate in HMPA, 1,1-diphenylethylene and tetraphenylethylene are reduced directly at a mercury electrode.[74]

**Table 14.** The reduction of alkenes by electrolysis in HMPA and methylamine.

| Medium | Proton donor | Alkene | Reduction product | Refs. |
|---|---|---|---|---|
| LiBr, HMPA | without donor | $(C_6H_5)_2C{=}CH_2$ | $[(C_6H_5)_2C(CH_2)_2C(C_6H_5)_2]^{2-*}$ | [71] |
| NaI, HMPA | without donor | $(C_6H_5)_2C{=}C(C_6H_5)_2$ | $[(C_6H_5)_2C{-}C(C_6H_5)_2]^{2-}$ | [71] |
| LiCl, HMPA | $C_2H_5OH$ 67 mole % | $(CH_3)_2C{=}C(CH_3)_2^{2*}$ | $(CH_3)_2CHCH(CH_3)_2$ | [44] |
| LiCl, methylamine | without donor | 1-octene | octane 51%$^{3*}$ | [72] |
| LiCl, HMPA | $C_2H_5OH$ 5–50 vol.% $C_3H_7OH$ 10–50 vol.% | cyclo-octa-1,5-diene | cyclo-octane, cyclo-octene$^{4*}$ | [73] |

Note: *) hydrolysis gave a high yield of tetraphenylbutane; 2*) the alkene $(CH_3)_2C = C(CH_3)_2$, which shows steric hindrance, is reduced in 30% yield at practically the same rate as hex-1-ene and hex-2-ene; 3*) the rest is the starting material (2% in unchanged form, 47% in the isomerised form); 4*) the proportion of cyclo-octene increases on going from ethanol to propanol and with decrease in the concentration of alcohol and increase in the current density.

It is of interest to compare the reactivities of alkene and aromatic bonds towards solvated electrons. Table 14 shows that in a number of cases only alkene bonds are reduced. This is characteristic of short alkene bonds¶. Thus the main product of the reduction of styrene in a solution of lithium chloride in methylamine (proton donor–solvent) is ethylbenzene (~70%),[72] and allylbenzene gives n-propylbenzene. If a stronger proton donor (ethanol) is added, the aromatic ring begins to be hydrogenated instead of the alkene bond, and the main product of the reduction of allylbenzene is 2,5-dihydroallylbenzene. The highest selectivity in methylamine in the presence of ethanol was achieved[72] for 5-phenylpent-2-ene, which gave 83% 2,5-dihydro-5-phenylpent-2-ene.

## 3. Ketones

Other compounds difficult to reduce are aliphatic ketones, which are reduced at potentials more negative than −2.0 V (s.c.e.).

A number of ketones illustrate another characteristic feature of the reduction of organic compounds by solvated electrons, namely the high stereospecificity of the process. In particular, the products of the reduction of alkylcyclohexanones and alkylcyclopentanones are alcohols in two stereoisomeric forms. Preparative data for these compounds are given in Table 15. The proton donor in all cases was ethanol.

**Table 15.** Reduction of alkylcyclopentanones and alkylcyclohexanones by solvated electrons generated in HMPA.

| No. | Ketone, mass% in the catholyte | Ketone : Donor | Electrode | Current efficiency, % | *trans*-Isomer, % | Method of reduction* | Refs. |
|---|---|---|---|---|---|---|---|
| 1 | 2-Methylcyclopentanone, 2 | 1:2 | copper | 83.5 | 90.2 | 2 | |
| 2 | 2-Methylcyclopentanone, 2 | 1:2 | copper | 88 | 90.6 | 1 | |
| 3 | 2-Methylcyclopentanone, 0.5 | 1:4,5 | platinum | 56.2 | 86.4 | 2 | [76] |
| 4 | 2-Methylcyclopentanone, 1 | 1:4,5 | copper | 78.5 | 93.7 | 2 | |
| 5 | 2-Ethylcyclopentanone, 2 | 1:2 | copper | 71.7 | 93.4 | 2 | |
| 6 | 2-Ethylcyclopentanone, 2 | 1:2 | copper | 84.8 | 89.3 | 1 | |
| 7 | 2-Methylcyclopentanone | 1:1 | copper | polymer | | 2 | |
| 8 | 4-t-Butylcyclohexanone | 4 mole % alcohol | platinum | 87 | 95 | 1 | [77] |
| 9 | 3,3,5-Trimethylcyclohexanone | 10 mole % alcohol | $5.9 \times 10^{-2}$ A cm$^{-2}$ | 50 | 91 | 1 | |

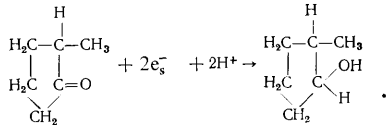
*1) The total quantity of substance to be reduced (and the proton donor) was added to the catholyte, and electrolysis was carried out until the stable colour of solvated electrons appeared; 2) the starting material (and the proton donor) was added to the catholyte containing previously generated electrons; the quantity of starting material added left a slight excess of solvated electrons; the whole procedure was repeated many times; Nos.1–7—sodium bromide; Nos.8 and 9—lithium chloride.

Table 15 shows that the cathode material and the method of reduction have no influence on the isomeric composition of the alcohol (the *trans*-form predominates†), whereas the electrode reduction gives a mixture of *trans*- and *cis*-carbinols, the ratio of which depends on the electrolysis conditions.[76] This indicated that in all cases the ketones are reduced by solvated electrons generated at the cathode, and this is confirmed by

¶ This agrees with data[75] which show that α-alkenes from pentene to decene are more difficult to reduce by metallic sodium in liquid ammonia than a longer alkene.

†High stereospecificity was also observed in the reduction of stilbenes in monoglyme by solvated electrons obtained by dissolving potassium; *trans*- and *cis*-stilbenes $C_6H_5CH = CHC_6H_5$ give the same radical-anion with the *trans*-configuration.[78]

the polarisation curves(Fig.6). Curve *1*, recorded in the presence of methylcyclopentanone and ethanol, lies in the range of generation potentials of solvated electrons (curve *2*). The slight displacement of the curve towards negative potential values in the presence of the ketone is due to the passivation of the surface as a result of the polymerisation of reduction products. Fig.6 gives for comparison curve *3*, corresponding to the case where the generation of electrons is accompanied by a second cathodic process, namely the cathodic liberation of hydrogen. Thus the reduction of cyclic ketones takes place according to the scheme



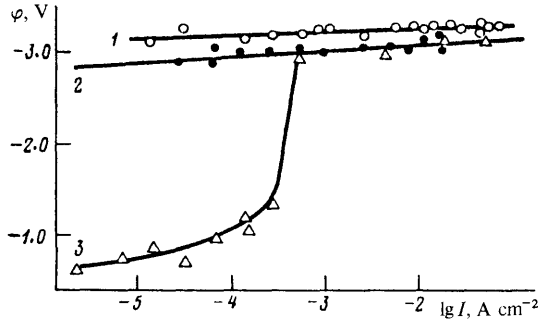
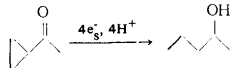



**Figure 6.** Dependence of the potential $\phi$, V (s.c.e.) on the current density at a stationary copper electrode in HMPA at 25 °C: *1*) lithium chloride 0.2 M + methylcyclopentanone $1.8 \times 10^{-2}$ M + ethanol $3.1 \times 10^{-2}$ M; *2*) lithium chloride 0.2 M; *3*) lithium chloride 0.1 M + sulphuric acid $2.2 \times 10^{-2}$ M.[76]

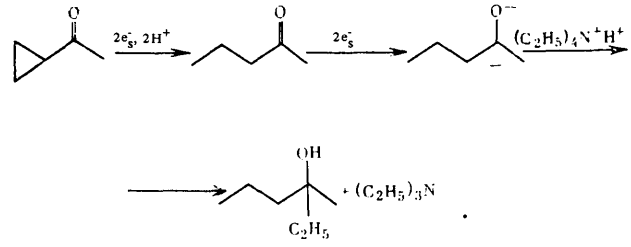
Similarly, solvated electrons generated at a cathode in a solution of lithium chloride in methylamine have been used[79] to reduce a number of ketones to the corresponding alcohols, namely heptan-2-one, pentan-3-one, cyclohexanone, and cyclopentanone. Electrons obtained by dissolving lithium, sodium, and potassium in HMPA have been used to reduce the ketone $C_6H_{13}COCH_3$, with t-butyl alcohol as proton donor.[80]

Alkali metals in liquid ammonia have been used[81] to reduce various substituted bicyclohexanones (bicyclo[3,1,0]hexa-3-en-2-ones).

The behaviour of acetylcyclopropanes deserves special examination. The reduction by an active metal in liquid ammonia takes place with opening of the ring:[82,83]



If the same reaction is carried out with electrochemically generated solvated electrons at a mercury or platinum cathode in liquid ammonia using tetraethylammonium tetrafluoroborate as background electrolyte, the chief electrolysis product is 3-methylhexan-3-ol. It is suggested that in this process the tetraethylammonium cations can act as an alkylating agent.



## 4. Carboxylic Acid Derivatives—Amides, Nitriles, and Esters

Electrochemically generated solvated electrons have been used to reduce various other organic compounds.

The data for aliphatic amides are given in Table 16.

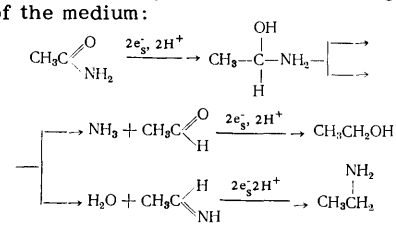
Table 16. The reduction of aliphatic amides by solvated electrons generated at a cathode.

| Medium | Proton donor | Amide | Reduction product, % | Refs. |
|---|---|---|---|---|
| LiCl + HMPA | acetic, oxalic, hydrochloric acids | $CH_3CONH_2$ | ethanol, ethylamine* | [84] |
| LiCl + methylamine | solvent | $CH_3(CH_2)_4CONH_2$ | alcohol, 58 | |
| | | $CH_3(CH_2)_6CONH_2$ | ditto, 59 | |
| | | $CH_3(CH_2)_{12}CONH_2$ | » 92 | |
| | | $CH_3(CH_2)_{11}CONH_2$ | » 86 | |
| | | $CH_3(CH_2)_{16}CONH_2$ | » 79 | |
| | | $CH_3(CH_2)_4CONHCH_3$ | » 51 | [79, 85] |
| | | $CH_3(CH_2)_6CONHCH_3$ | » 81 | |
| | | $CH_3(CH_2)_6CON(CH_3)_2$ | » 93 | |

*Decrease in temperature and the current density, and increase in the acidity, increase the proportion of amine.

Table 16 shows that solvated electrons can reduce aliphatic amides to alchols in good yield. In a medium of methylamine, the alcohol is formed if the solvent itself acts as proton donor. When ethanol, which is a stronger proton donor, is added to methylamine, the yield of alcohol decreases sharply, and the aldehyde becomes the main reaction product.[79,85]

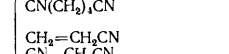
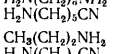
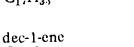
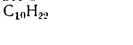
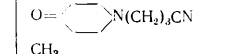
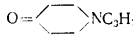
In the reduction of acetamide in HMPA, the reduction products are ethylamine and ethanol. When the process is carried out at room temperature, the main reduction product is ethanol, but at a lower temperature (~11 °C), the two products are formed in approximately equal quantities. A low current density and more acidic proton donors (for example hydrogen chloride) also favour the formation of the amine. To explain the observed regularities, it was suggested that the first stage of the reduction is the formation of an unstable aminoalcohol, which undergoes decomposition depending on the acidity of the medium:



Ethanol is formed in basic catalysis, whereas another route, giving the amine, is followed preferentially in an acidic medium.

Published data on the reduction of nitriles and dinitriles are summarised in Table 17#.

**Table 17.** Reduction of nitriles and dinitriles by solvated electrons.[86–89]

| Method of generating electrons | Nitrile | Product (%) |
|---|---|---|
| Cathodic generation in a solution of lithium perchlorate in HMPA* | $CH_3CN$ | $C_2H_5NH_2$ |
| | $CN(CH_2)_4CN$ | $H_2N(CH_2)_6NH_2$<br>$H_2N(CH_2)_5CN$ |
| Ditto | $CH_2{=}CH_2CN$ | $CH_3(CH_2)_2NH_2$ |
| | $CN{-}CH_2CN$ | $H_2N(CH_2)_2CN$<br>$H_2N(CH_2)_3NH_2$ |
| Solution of potassium in hexamethylphosphortriamide[2]* | $C_7H_{15}CN$ | $C_7H_{16}$ (80) |
| | $C_{10}H_{21}CN$ | $C_{10}H_{22}$ (90) |
| | $C_{17}H_{35}CN$ | $C_{17}H_{33}$ (80) |
| | $H_{13}C_6CH(CN)CH_2{=}CHCH_2$ | dec-1-ene (32)<br>$C_{10}H_{22}$ (32) |
| | $(CH_3)_2C(CN)C_7H_{15}$ | 2-methylnonane (89) |
| |  |  (76) |
| | $CH_3CH(CH_2)_2C(CH_2)_2CN(CH_3)_2$ | 2,5-dimethylhexane (76) |
| | $PhCH(CN)C_4H_9$ | allylbenzene (34) |
| | |  (26) |
| | $PhC(C_4H_9)(CN)C_4H_9$ | $PhCH(C_4H_9)_2$ (56) |
| | |  (16) |
| | $PhCH_2C(CH_3)(CN)CH_3$ | $PhCH_2CH(CH_3)_2$ (80–85) (with and without alcohol) |
| Solution of sodium in liquid ammonia[3]* | $Ph_3CCN$ | $Ph_3CH$ (90) |
| | $Ph_2CHCN$ | $Ph_2CH_2$ (76) |
| | $PhCH_2CN$ | $PhCH_3$ (90) |
| | $PhCN$ | $C_6H_6$ |
| | $[(CH_3)_2NC_6H_4]_3CCN$ | $[(CH_3)_2NC_6H_4]_3CH$ (93) |
| Solution of lithium in liquid ammonia |  |  (43) |
| | | $CH_3CH(CH_3)CH_2CH_3$ (37) |
| | | $CH_3CH_2CH(CH_3)CH_3$ (18) |
| Solution of lithium in ethylamine | $n\text{-}C_{12}H_{25}CN$ | $n\text{-}C_{12}H_{26}$ (35)<br>$n\text{-}C_{13}H_{27}NH_2$ (65) |
| Cathodic generation in a solution of lithium chloride in ethylamine | dehydroabietonitrile<br>cycloheptyl cyanide<br>n-octyl nitrile | dehydroabietane<br>cycloheptane<br>n-octane |

Note. *) Sufficient nitrile and ethanol (proton donor) was added by means of a micro-burette to a solution in which solvated electrons had previously been generated, to leave a slight excess of electrons; the procedure was repeated many time; 2*) the co-solvent t-butyl alcohol was used as proton donor, although in the authors' opinion the role of donor may be played by HMPA; 3*) the alkali metal was dissolved in ammonia, the nitrile was added, the ammonia was removed, and hydrolysis was carried out.

#The reduction of nitriles to amines also takes place by direct electrode reduction in solutions of hydrochloric and sulphuric acids in ethanol at palladium or nickel black cathodes (benzonitrile to benzylamine, and benzyl cyanide to β-phenylethylamine).[90]

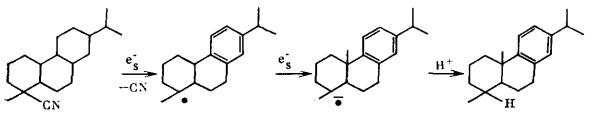
Solvated electrons, generated at a cathode or obtained by dissolving an alkali metal, have been used to reduce nitriles. Table 17 shows that in general, two reactions may take place: decyanation to give the hydrocarbon

$$RCN + 2e_s^- + 2H^+ \rightarrow RH + HCN$$

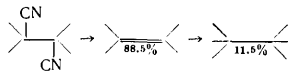
and reduction to the amine

$$RCN + 4e_s^- + 4H^+ \rightarrow RCH_2NH_2 \ .$$

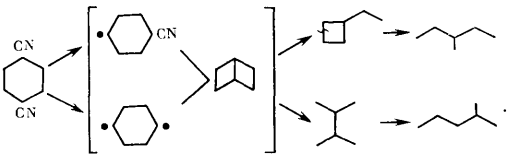
The amine group formed is inert towards solvated electrons. Judging from available data on reduction by solvated electrons, the more characteristic reaction is the removal of the nitrile group (decyanation), which probably takes place via a radical-anion stage. Thus the following scheme has been proposed[91] for the reduction of dehydroabietonitrile by sodium in liquid ammonia:



Nitrile groups on neighbouring carbon atoms are removed with the preferential formation of carbon–carbon multiple bonds, for example:




Interesting transformations are undergone by 1,4-dicyanocyclohexane under the influence of solvated electrons:[88]



The final reaction products are 3-methylpentane and 2-methylpentane.

The nitrile group is apparently more reactive towards solvated electrons than the alkene bond or the bonds of the benzene ring, but the latter may be partly hydrogenated after the nitrile group has been reduced (Table 17).

Solvated electrons also reduce esters.[92] In particular, dimethyl adipate gives hexane:

$$CH_3OC(=O)(CH_2)_4C(=O)OCH_3 \xrightarrow[-2H_2O]{12H^+,\ 12e_s^-} C_6H_{14} + 2CH_3OH$$

that is the reduction takes place with rupture of the C–O bond. There are no published quantitative data on this reaction.

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The material of the present review shows that electrochemically generated solvated electrons can be used successfully to reduce various organic compounds, many of which are electrochemically inactive, that is at the potentials attainable in polar solvents (between −2.5 V and −2.8 V, s.c.e.) there is practically no electron exchange between an electrode and the molecules of these organic substances. Thus the electrochemical generation of solvated electrons extends the possibilities in preparative electrochemical synthesis.

Another advantage of this method is that the actual generation of the solvated electrons can be carried out with high current densities, irrespective of the concentration of organic substance in the solution. This feature is important when it is necessary to carry out the exhaustive reduction of a substance present in solution at a low concentration. Thus the use of solvated electrons can be regarded as one possible way of intensifying electrochemical processes.

The first work on the generation of solvated electrons was carried out in liquid ammonia, and slightly later, HMPA began to be used as solvent. Both of these solvents are inconvenient to use. Ammonia can be used only at low temperatures of about −30 °C, and HMPA has a high boiling point, so that the separation of pure reduction products from it is difficult. In this connection it is worth noting recently published data on the possibility of generating electrons in solutions containing a large quantity of protogenic solvents, or even in aqueous solutions, containing 25–40% tetrabutylammonium salts. The change to these media simplifies considerably the procedure for generating solvated electrons, making it comparable with the ordinary electrochemical process. This version of electroreduction by solvated electrons should apparently find preparative application in laboratory practice and in various industrial processes.

The reduction of organic substances with the participation of solvated electrons can be regarded as a particular case of reactions involving electron carriers, which may be either organic or inorganic compounds. The use of solvated electrons, however, has at least two advantages: it is not necessary to introduce additional reagents into the reaction mass, and in preparative electrolysis this facilitates the separation of the reaction products; and there are processes such as, for example, the reduction of amides or certain aromatic compounds, which can be carried out only using solvated electrons. From these viewpoints alone, the use of solvated electrons in the electrosynthesis of organic substances appears promising and worthy of further study.

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# Ferrocenyl Carbonium Ions and Related Cationic Complexes. Structure and Stabilisation Mechanism

A.A.Koridze

The review presents data on the structure and mechanism of the stabilisation of ferrocenyl carbonium ions and related cationic complexes with different types of hydrocarbon ligands. The results obtained in the study of complex carbonium ions by X-ray diffraction, $^{57}$Fe Mössbauer spectroscopy, and $^{1}$H, $^{13}$C, $^{19}$F, $^{57}$Fe, and $^{187}$Os NMR are compared. It is shown that the ability of the metal atom to interact directly with the carbonium ion centre generated in the β-position relative to it is a general property of transition metal complexes.
The bibliography includes 132 references.

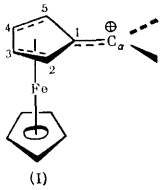
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## I. INTRODUCTION

Over a quarter of a century has elapsed since the discovery of the unusually high stability of α-ferrocenylcarbonium ions.[1] It was found subsequently that the enhanced stability is a characteristic property of complex carbonium ions in which the transition metal is present in the β-position relative to the carbonium ion centre. α-Ferrocenylcarbonium ions remain the most thoroughly investigated among complex carbonium ions because of their comparatively high stability, the ready availability of ferrocene, and the wide variety of its chemical behaviour.

Throughout all these years, a lively controversy has continued concerning the structure and mechanism of the stabilisation of the α-ferrocenylcarbonium ions (see the earlier reviews[2-6]). In the explanations put forward for the stability of these ions, one can see two main concepts differing in the role which the transition metal atom plays in the stabilisation. According to one of them, the high stability of the carbonium ions (I) is achieved by the overlap of the *d* orbitals of the metal atom with the unoccupied *p* orbitals of the α-carbon atom. On the other hand, it has been claimed that the delocalisation of the positive charge of the ferrocenyl group takes place via a system of carbon–carbon bonds without the direct involvement of the iron atom in the stabilisation of the carbonium ion centre.




(I)

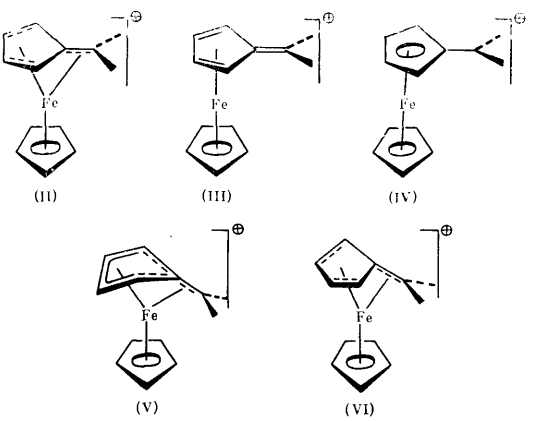
A wide range of physicochemical methods have been used to solve the problem of the structure and mechanism of the stabilisation of α-ferrocenylcarbonium ions. The data obtained recently have led to a considerable advance in our understanding of the causes of the enhanced stability of these cationic complexes. However, there are no reviews in the literature in which the experimental data obtained by different methods have been examined critically.

We therefore thought it useful to discuss the available data on the structure and mechanism of the stabilisation of ferrocenylcarbonium ions and also, bearing in mind the general nature of the problem, the corresponding information about related complex cations.

## II. FERROCENYLCARBONIUM IONS

### 1. Structural Models of α-Ferrocenylcarbonium Ions

The unusually high ability of the ferrocenyl group to stabilise the neighbouring carbonium ion centre was demonstrated at an early stage in ferrocene chemistry. In particular, this was manifested by the high rate of solvolysis of α-acetoxyalkylferrocenes (comparable to that of trityl acetate)[1,7,8] and the ease of addition of weak acids to α-vinylmetallocenes.[9] Hill and Richards[7] suggested that structure (II) can reasonably explain the high stability of α-ferrocenylcarbonium ions. In this structure the $FeC_5H_5$ fragment is displaced towards the exocyclic carbon atom and the *d* orbitals of the metal atom overlap the *p* orbital of the $C_\alpha$ atom.




(II) (III) (IV) (V) (VI)

According to Traylor,[10,11] there is no need to postulate the direct participation of the iron atom in stabilisation to account for the experimental data and the best description of the structure of α-ferrocenylcarbonium ions is provided by the

resonance hybrid (III) ↔ (IV) with the predominant contribution by the canonical fulvene structure (III). Subsequently this concept was invoked to account for the mechanism of the stabilisation of other complex carbonium ions.

Both models have been frequently criticised. The criticism of model (II) is based on data obtained in a comparative $^1$H NMR study of various α-ferrocenylcarbonium ions—of the kind for which a shift of the $FeC_5H_5$ fragment is possible and others where such a shift is prevented by the presence of a heteroannular bridge.[12] Traylor's model[10,11] has been criticised because the metal atom in structure (III) [which makes a dominant contribution to the (III) ↔ (IV) resonance hybrid] has a 16-electron configuration unusual for such an atom. Furthermore, structure (III) was proposed as a model for α-ferrocenylcarbonium ions on the basis of a comparison of $^1$H NMR data for these cations and related tricarbonyliron(η-cyclobutadienyl)-substituted carbonium ions for which $\eta^3$-binding of the cyclic ligand has been erroneously postulated.[13] However, this structure was rejected after an X-ray diffraction study of the $BF_4^-$ salt of the bis[tricarbonyliron-(η-cyclobutadienyl)]benzyl cation.[14]

A further two structural models of α-ferrocenylcarbonium ions, in which there is a direct Fe–$C_\alpha$ interaction, have been proposed. These are Cais's structure (V) with a non-planar cyclic ligand [bent at the C(II) and C(V) atoms][2,3] and structure (VI) in which the exocyclic bond is displaced from the plane of the five-membered ring and inclines towards the metal atom.[15] According to Cais, model (V) explains satisfactorily both the data on the solvolysis of ferrocene derivatives and the $^1$H NMR data for α-ferrocenylcarbonium ions. However, a distortion of the cyclic ligand of this kind has not been observed in any of the X-ray diffraction studies of both cationic and uncharged cyclopentadienyl or fulvene metal complexes.

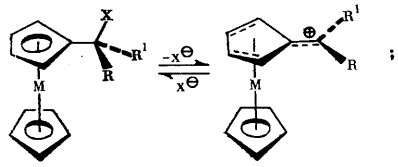
Model (VI) has been proposed on the basis of a calculation for $[FcCH_2]^\oplus$ (Fc = ferrocenyl) by the extended Hückel method.[15] According to the calculation, a 40° inclination of the C(I)–$C_\alpha$ bond in the direction of the iron atom corresponds to the minimum energy and the five-membered rings deviate from a parallel arrangement by 10°. The distortion of the fulvene ligand (the substituted ligand in α-metallocenylcarbonium cations is frequently regarded as a fulvene ligand[7,16]) is a consequence of the interaction of the unoccupied π* molecular orbital of the fulvene ligand with the $d_{z^2}$ orbital of iron, which is non-bonding in ferrocene. According to the calculation, in contrast to model (VI), the model with a planar fulvene ligand should have a triplet ground state.

Model (VI) is consistent with many experimental data. However, one should note that a subsequent calculation[17] for $[FcCH_2]^\oplus$ by an analogous method led to a structure in which the angle of inclination of the C(I)–$C_\alpha$ bond is only 6°.

## 2. Kinetics and Stereochemistry of Solvolytic Reactions

After the first communications about the hydrolysis of the carbinols of the ferrocene series via the $S_N1$ mechanism, demonstrating the high stability of α-ferrocenylcarbonium ions,[1,8] several groups of investigators measured the rate of solvolysis in order to elucidate the role of the metallocenyl group in the acceleration of these reactions.[7,10,11,18–23]

Together with a high rate of the reactions of the metallocenyl-substituted substrates in solvolysis, the preferential *exo*-elimination of the leaving group was then demonstrated (the attack by the nucleophile on the carbonium ion also takes place in the *exo*-position).[8,18]

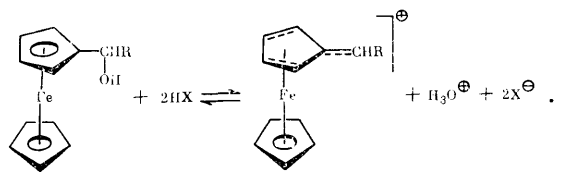


M = Fe, Ru, Os.

The increase of the solvolytic reaction in the series of iron, ruthenium, and osmium derivatives is regarded as evidence for the direct nucleophilic cooperation of the metal atom in these reactions. The stereochemical result of these reactions is also explained by the direct involvement of the metal atom.[8,18] On the other hand, the high rate of these reactions has been attributed to the effect of σ,π-conjugation (vertical stabilisation) and the stereochemical result has been attributed to steric causes.[10,11,21,22]

In considering the kinetic data it has usually been assumed that the α-ferrocenylcarbonium ion is closely related to the transition state in the heterolytic process. However, a very interesting observation has been made: the thermodynamic stability of α-ferrocenylcarbonium ions is much higher than would follow from the rate of their formation in solvolytic reactions.[24]

The thermodynamic stabilities of a series of α-ferrocenylcarbonium ions have been determined in a quantitative study of the ionisation equilibria involving ferrocenylcarbonium ions in aqueous solutions of inorganic acids:



The equilibrium constants of the above reaction have been determined in $H_2SO_4(HClO_4)$–$H_2O$ systems. The $pK_{R^+}$ were obtained from linear plots of lg $[R^+]/[ROH]$ against the acidity function $H_{R^+}$.

The discrepancy between the data for the stability of ferrocenylcarbonium ions obtained from measurements of the equilibrium constants and the reaction rates suggests that a significant electronic and evidently a structural rearrangement of the ferrocenyl group takes place in the pathway from the transition state to the α-ferrocenylcarbonium ions in the heterolytic process.[24]

## 3. X-RAY DIFFRACTION STUDY OF THE SALTS OF COMPLEX CARBONIUM IONS

It was to be expected that X-ray diffraction study of the salts of α-ferrocenylcarbonium ions or related cationic complexes would provide a final unambiguous answer to the question whether there is a direct interaction of the metal atom with the carbonium ion centre. However, the problem was not found to be quite so simple.

No significant interaction of any kind between the iron atoms and the carbonium ion centre has been observed in the structure of the $BF_4^-$ salt of bis[tricarbonyliron(η-cyclobutadienyl)]benzyl cation,[14] where the Fe...$C_\alpha$ distances amounted to 2.85 and 2.94 Å. The $C_\alpha$ atom is coplanar with the cyclobutadiene rings, which have been somewhat rotated (by 5° and 8°) relative to the molecular plane; the benzene ring has undergone a rotation by 43°. This shows that the organometallic groups make a larger contribution to stabilisation than the benzene ring.

Nor has a significant Fe...$C_\alpha$ interaction been observed in the $BF_4^-$ salt of the ferrocenyldiphenylcyclopropenyl cation.[25] The Fe...$C_\alpha$ distance is 2.96 Å and the angle of inclination of the C(I)–$C_\alpha$ atom in the direction of the iron atom is 6.3°. The deviation of the $C_\alpha$ atom relative to the plane of the ligand by 0.16 Å exceeds only slightly the value (~0.1 Å) observed in certain uncharged ferrocene derivatives. One cannot therefore agree with the authors' claim[25] that the Fe–$C_\alpha$ interaction takes place in this complex. Furthermore, bearing in mind the aromatic character of the cyclopropenyl cation, one can hardly expect any significant Fe–$C_\alpha$ interaction, leading to the delocalisation of the positive charge.

In the study of the structure of the $BF_4^-$ salt of the diferrocenylmethyl cation it was observed[26,27] that the $C_\alpha$ atom has deviated from the plane of the five-membered rings but the Fe...$C_\alpha$ distances have been reduced to 2.69 and 2.81 Å, which corresponds to inclinations of the exocyclic bonds towards the iron atoms by 19.9° and 17.9° respectively. The authors suggest that the observed deviations may be the result of the interaction of the *d* electrons of the iron atom with the fulvene system, although the Fe...$C_\alpha$ distances are too large to permit the presence of a strong bond.

Yet another dinuclear complex with unequal Fe...$\overset{\oplus}{C}$H distances (2.59 and 2.72 Å) is $\{[Fe(\eta\text{-}C_5H_5)(CO)_2CH_2]_2CH\}.[BF_4]$.[28] In the precursor of this complex $[Fe(\eta\text{-}C_5H_5).(CO)_2CH_2]_2CH_2$ (the complex is generated from the latter by the abstraction of a hydride ion) the Fe...$C_\beta H_2$ distances are 3.07 Å.[29] It has been suggested that the difference between the Fe...$\overset{\oplus}{C}$H distances in the cationic complex are due to forces associated with the crystal packing.

The results of a study of the structure of the $BF_4^-$ salt of the ferrocenyldiphenylmethyl cation were published in 1979.[30] The angle of inclination of the C(I)–$C_\alpha$ bond in this complex is 20.7° and the Fe...$C_\alpha$ distance is 2.715 Å.† The metal atom occupies an asymmetric position under the substituted ring, being displaced somewhat (by 0.008 Å) in the direction of the exocyclic $C_\alpha$ atom. As a result, the Fe–C(1) distance is somewhat shorter (2.009 Å) and the Fe–C(4) and Fe–C(5) distances are somewhat longer (2.095 and 2.085 Å) than the average length of the bond between the iron atom and the carbon atoms of the unsubstituted ring (2.056 Å). The planes of the five-membered rings are at an angle of 9.3°. The length of the exocyclic C(1)–$C_\alpha$ bond (1.416 Å) is significantly smaller than would be expected for a single bond between $sp^2$-hybridised carbon atoms (1.48 Å) indicating an appreciable proportion of double bond character. According to Behrens,[30] the structure can be fully regarded as one corresponding to the diphenylfulvenylcyclopentadienyliron cation.

Here it is appropriate to recall that the possibility of an appreciable deviation of the exocyclic bond of the fulvene ligand had been demonstrated earlier in a study of diphenylfulvenechromium tircarbonyl;[32] a similar deviation of the *exo*-bond has been observed recently for the complex $C_5H_5FeC_2B_9H_{10}CHC_6H_5$.[33]

Compared with the complex $(OC)_3CrC_5H_4C(C_6H_5)_2$, in which the angle of inclination of the *exo*-bond is 31°, in the zwitter-ionic chromium complex $(OC)_3\overset{\ominus}{C}rC_5H_4CH{=}\overset{\oplus}{N}(CH_3)_2$ with a planar imine group the corresponding angle of inclination is only 10°.[34] The decrease of the degree of deviation of the fulvene ligand from planarity with increasing ability of the substituent to delocalise the positive charge on the $C_\alpha$ atom also follows from data obtained for the complex $FcCH{=}\overset{\oplus}{N}(CH_3)_2$ where the "distortion is minimal".[35] The influence of complex formation with the metal and of the nature of the substituent at the $C_\alpha$ atom on the distortion of the fulvene ligand and on the barrier to rotation about the *exo*-bond has been examined.[35]

Thus structural studies on salts of α-ferrocenylcarbonium ions and related complexes have provided much valuable information about the structure of these interesting systems in the crystal state and the results of Cais et al.[26] and Behrens[30] can be regarded as evidence for the direct Fe–$C_\alpha$ interaction. However, it remains obscure to what extent the Fe...$C^\oplus$ distances found for the complex cations, which occur in the wide range from 2.59 to 2.96 Å, should be regarded as "bonding" and what the situation is in this respect on passing from the crystal to the solution. It would be desirable to answer this question also in connection with the fact that hitherto there have been no structural data for the carbonium ion $[FcCH_2]^\oplus$ in which the strongest Fe–$C_\alpha$ bond is to be expected.

## 4. $^{57}$Fe Mössbauer Spectroscopy

The study of frozen solutions (137 K) of the carbonium ion $[FcCH_2]^\oplus$ in concentrated sulphuric acid and of the carbinol $FcCH_2OH$ in benzene by $^{57}$Fe Mössbauer spectroscopy[36,37] showed that the isomer shifts δ of the complexes differ little and are close to that for ferrocene (0.56, 0.57, 0.53 mm $s^{-1}$ respectively). According to the author's data, another parameter, namely the quadrupole splitting Δ, for the carbinol $FcCH_2OH$ is the same as for ferrocene, whereas Δ for the carbonium ion is greater by 15% than for the carbinol—1.99 and 2.29 mm $s^{-1}$ have been quoted for $FcCH_2OH$ and $[FcCH_2]^\oplus$. It is known that the chemical shifts for the ferrocene derivatives vary little and are observed in the range 0.48–0.60 mm $s^{-1}$ at 80 K; the quadrupole splittings are somewhat more sensitive to the influence of the substituent (2.05–2.55 mm $s^{-1}$) and diminish as the electron-accepting properties of the substituent are enhanced.[38,39] Accordingly, the substituent in model (IV) of α-ferrocenylcarbonium ions should manifest pronounced electron-accepting properties, which would diminish Δ. Model (II) with participation of the iron atom, in which one of the cyclopentadienyl ligands has been substituted by the fulvene ligand, linked to the metal atom the six carbon atoms, is consistent with experimental data according to Dannenberg and co-workers.[36,37]

A series of studies have been published recently (see Roberts and Silver[40] and the references quoted therein) concerning the application of Mössbauer spectroscopy to the study of derivatives of ferrocene and α-ferrocenylcarbonium ions. Neshvad et al.[41] studied the carbonium ion $[FcCH_2]^\oplus$ and $[FcCHCH_3]^\oplus$ and criticised the earlier investigations.[36,37] It was found that Δ for $FcCH_2OH$ and $[FcCH_2]^\oplus$ are not 1.99 and 2.29 mm $s^{-1}$ but 2.40 and 2.70 mm $s^{-1}$ respectively.[41] Furthermore, in discussing their own data, Dannenberg and Richards[36] used an erroneous, unduly low, value of Δ for ferrocene.

Overall, the reasoning the conclusions arrived at by both groups of investigators were analogous. A new factor in the study of Neshvad et al.[41] is that, in contrast to $[FcCH_2]^\oplus$, for which the Fe–$C_\alpha$ interaction has been postulated, in the tertiary carbonium ion $[FcC(CH_3)_2]^\oplus$ the possibility of this interaction is ruled out on the grounds of the similarity of the values of δ and Δ for this complex (0.51 and 2.41 mm $s^{-1}$ respectively) and for ferrocene (0.53 and 2.42 mm $s^{-1}$). It has been suggested that the stabilisation in the complex

†It is remarkable that the Fe...$C^\oplus$ distances found in a number of studies,[26–28,30] are close to that between the bridging μ-CO ligand and the most remote iron atom in the cluster $[Fe_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}CO)]^{2\ominus}$; the distance 2.72(1) Å is believed to correspond to the presence of a bond between them.[31]

$[FcC(CH_3)_2]^{\oplus}$ is achieved through the inductive and hyperconjugation influences of the two methyl groups and also the resonance influence of the cyclopentadienyl ligand (see, however, Section II).

### 5. $^1$H NMR Spectroscopy

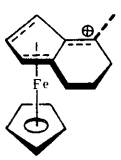
$^1$H NMR spectroscopy makes it possible to detect readily the formation of α-ferrocenylcarbonium ions when the traditional precursors of these ions, namely α-ferrocenylcarbinols[42-45] and α-vinylferrocenes[46] are treated with acids, usually $CF_3COOH$ or $H_2SO_4$.

The formation of α-ferrocenylcarbonium ions is accompanied by a downfield shift of the signals due to the cyclopentadienyl protons. The greatest shift is then undergone by the signals of the H(3,4) protons of the substituted ring, while the H(2,5) protons are less deshielded [in contrast to acylferrocenes and other ferrocene derivatives with substituents exhibiting the $-R$ effect, in which the H(2,5) protons are more deshielded than the H(3,4) protons]. Thus, signals at $\delta$ = 5.45 ($CH_2$), 4.72 [H(2,5)], 6.32 [H(3,4)], and 5.27 ($C_5H_5$) p.p.m. have been observed[45] in the spectrum of a solution of the cation $[FcCH_2]^{\oplus}$ in $CF_3COOH$ ($\delta$ = 4.04 p.p.m. for ferrocene in $CCl_4$).

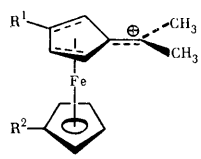
The difference between the relative shieldings of the H(2,5) and H(3,4) protons depends on the character of the substituent at the carbonium ion centre $C_\alpha$ and diminishes with increase of the ability of the substituent to delocalise the charge. For non-identical substituents at the $C_\alpha$ atom, four protons of the substituted ligand in the spectrum of α-ferrocenylcarbonium ions give separate signals, indicating that the rotation about the exocyclic $C(1)-C_\alpha$ bond is hindered.

The fact that the H(2,5) protons of the substituted ligand are more shielded in α-ferrocenylcarbonium ions (in contrast to, for example, acylferrocenes) has been regarded as evidence in support of model (II): when the $FeC_5H_5$ group shifts towards the $C_\alpha$ atom, its anisotropic effects leads to a greater shielding of the H(2,5) protons.[37]

To test the possibility of the displacement of the $FeC_5H_5$ fragment along the fulvene ligand, the carbonium ions (VII)–(X) have been investigated[12] assuming that such a shift is possible in the complexes (VII)–(IX) but not in the complex (X), where this is prevented by the heteroannular bridge consisting of three methylene units.



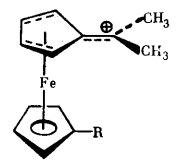
(VII)



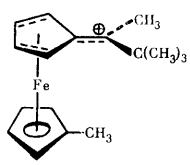
(VIII): $R^1 = R^2 = H$
(IX): $R^1 = R^2 = CH_3$
(X): $R^1, R^2 = (CH_2)_3$

The average difference $\Delta\nu$ between the shieldings of the H(2,5) and H(3,4) protons in the complexes (VII)–(X) is 72, 80, 86 and 65 Hz respectively, which is believed to be inconsistent with model (II) [a greater difference $\Delta\nu$ is expected if the model is applied to the complexes (IX) and (X)]. One can therefore assume that α-ferrocenylcarbonium ions undergo a deformation which is different from that postulated by the above model; otherwise one would have to assume that the metal–ring interaction and the character of the charge distribution in α-ferrocenylcarbonium ions and ferrocene differ significantly.

Data consistent with the distortion from planarity of the fulvene ligand have been published.[47] The protons of the alkyl-substituted ring in the carbonium ion (XI) are manifested in the $^1$H NMR spectrum by a single narrow signal, which indicates the ease of the relative rotation of the rings. However, the H(2,5) and H(3,4) protons of the methylcyclopentadienyl ligand give rise to two multiplets at $\delta$ = 4.78 and 5.15 p.p.m. in the spectrum of the cation (XII), which is believed to be due to the restriction of the rotation of the cyclic ligands as a consequence of the contact between the t-butyl group at the $C_\alpha$ atom and the methyl group of the $C_5H_4CH_3$ ligand.



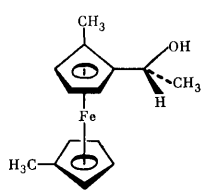
(XI): R = $CH_3$, $C_2H_5$, $CH(CH_3)_2$, $C(CH_3)_3$



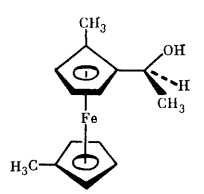
(XII)

Such a difference between the relative rotations of the ring in the isomeric complexes (XI, R = t-butyl) and (XII) was not to be expected for planar fulvene ligands. The spectroscopic differences between the isomeric cations noted above are therefore explained by the distortion of the fulvene ligand similar to that postulated in models (V) and (VI).

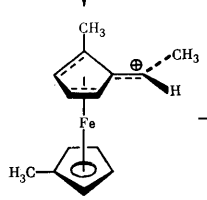
$^1$H NMR has been used to study the barrier to rotation about the exocyclic bond in α-ferrocenylcarbonium ions.[48] When the diastereoisomeric carbinols (XIII) and (XIV) are dissolved in acid, the isomeric carbonium ions (XV) and (XVI) are generated respectively and it is possible to follow the slow transformation of the carbonium ion (XV) into the sterically less strained isomer (XVI).



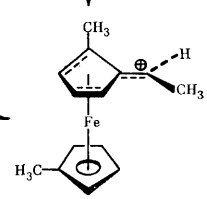
(XIII)



(XIV)



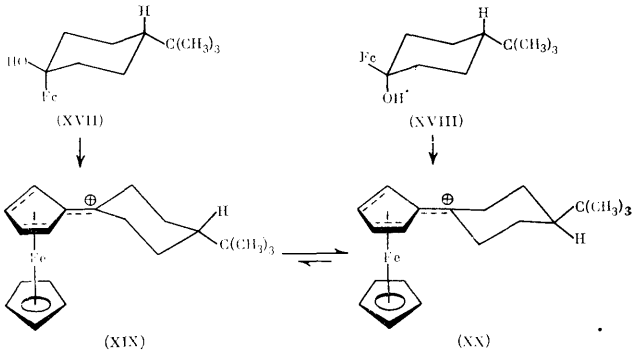
(XV)



(XVI)

The barrier to rotation about the $C(1)-C_\alpha$ bond is sufficiently large to detect the optically active carbonium ions generated from the enantiomeric carbinols *R*-(−)-$FcCH(OH).CH_3$ and *S*-(+)-$FcCH(OH)CH_3$; the racemisation of these ions has been investigated by the polarimetric method.[48]

The carbonium ions (XIX) and (XX) are formed from the tertiary carbinols (XVII) and (XVIII) respectively; the complexes isomerise slowly, giving rise to an equilibrium mixture consisting mainly (approximately 90%) of the carbonium ion (XX).



(XVII) (XVIII)

(XIX) (XX)

The lower stability of the carbonium ion (XIX) compared with (XX) has been explained by the more marked steric repulsion between the conformationally rigid t-butylcyclohexyl ring and the unsubstituted cyclopentadienyl ligand.[48]

The torsional barrier in the equilibrium (XIX) ⇌ (XX) between the tertiary carbonium ions is appreciably lower than in the equilibrium (XV) ⇌ (XVI) between the secondary carbonium ions (69.4 ± 2 and 88.7 ± 2.0 kJ mol$^{-1}$ respectively). Consequently the difference between the energy barriers to rotation about the C(1)–$C_\alpha$ bond is not determined by steric causes due to contacts between the substituents at the $C_\alpha$ atom and the unsubstituted ring in the transition state. It is believed that these differences reflect the role of the electronic factors characteristic of the substituents at the $C_\alpha$ atom.[48]

The estimated torsional barriers (~100 kJ mol$^{-1}$) in the α-ferrocenylcarbonium ions show that the exocyclic bond of the fulvene ligand does not have an appreciable double bond character and this is inconsistent not only with model (III) but also with the appreciable contribution of the canonical structure (III) to the (III) ↔ (IV) resonance hybrid.[48]

## 6. $^{13}$C NMR Spectroscopy

The study of α-ferrocenylcarbonium ions by $^{13}$C NMR showed that the signals of all the carbon atoms in the cyclic ligand have undergone a downfield shift compared with the neutral precursors, which indicates the delocalisation of the charge over the entire ferrocenyl unit.[49–56] The deshielding of the carbon nuclei in the ferrocenyl group is relatively insensitive to the nature of the substituents at the $C_\alpha$ atom, so that the ferrocenyl group makes the main contribution to the stabilisation of the carbonium ion.

The relative shielding of the C(2,5) and C(3,4) atoms in the $^{13}$C NMR spectra of α-ferrocenylcarbonium ions is the same as that of the H(2,5) and H(3,4) atoms: the signals of the nuclei in the 3,4-positions are less shielded. Thus signals at δ = 87.7 ($CH_2$), 110.6 [C(1)], 84.6 [C(2,5)], 94.4 [C(3,4)], and 82.3 ($C_5H_5$) p.p.m. have been observed in the spectrum of the cation $[FcCH_2]^\oplus$ (δ = 67.7 p.p.m. for ferrocene in dichloroethane). Similar relative shielding of the carbon atoms of the substituted ligand has been observed in the ferrocene derivatives FcR, where R = CHO, $COCH_3$, CN, or other substituents with a $-R$ effect.[57]

The cause of the smaller shielding of the C(3,4) atoms compared with C(2,5) may be the known sensitivity of the former to the $-R$ effect of the substituents in ferrocene derivatives.[57] Another factor which also favours the observed spectral picture may be the shift of the $FeC_5H_5$ fragment to the exocyclic $C_\alpha$ atom. Such a shift would weaken the bond between the metal atom and the C(3,4) carbon atoms and hence should entail a smaller shielding of the latter as a consequence of the diminution of the effect of the "coordination shift"#. At the same time the displacement of $FeC_5H_5$ towards the $C_\alpha$ atom should favour a greater shielding of the C(2,5) atoms as a consequence of the effect of the magnetic anisotropy of the $FeC_5H_5$ fragment.[37]

In the discussion of the $^{13}$C NMR spectra of α-ferrocenylcarbonium ions, attention was drawn to the relatively small downfield shift of the $C_\alpha$ signal on passing from carbinols to carbonium ions.[51] For example, on formation of the $[FcCH_2]^\oplus$, $[FcCHCH_3]^\oplus$, and $[FcCHC_6H_5]^\oplus$ carbonium ions from the corresponding carbinols, the quantities $\Delta\delta(^{13}C_\alpha)$ are 26.2, 52.1, and 49.9 p.p.m. respectively. On the other hand, they are much greater for organic systems, $\Delta\delta(^{13}C_\alpha)$ amounting to 127.4 p.p.m. in the case of the 3,5-$(F_3C)_2C_6H_3$·.$CH(OH)CH_3$/3,5-$(F_3C)_2C_6H_3\overset{\oplus}{C}HCH_3$ pair for example.[58] This difference between the $\Delta\delta(^{13}C_\alpha)$ for organometallic and organic systems may be the result of the more effective delocalisation of the positive charge in the organometallic carbonium ions and the occurrence of the metal–$C_\alpha$ interaction.

The $^{13}$C–$^1$H spin–spin interaction constants (SSIC) for α-ferrocenylcarbonium ions, which are in the range 160–165 Hz, are consistent with the $sp^2$ hybridisation of the $C_\alpha$ atom but not with the formation of the Fe–$C_\alpha$ σ-bond.[49,51–53,55]

## 7. The $^{57}$Fe NMR Chemical Shifts and the $^{13}$C–$^{57}$Fe Spin–Spin Interaction Constants for α-Ferrocenylcarbonium Ions

Since it is impossible to resolve the question of the mechanism of the stabilisation of α-ferrocenylcarbonium ions within the framework of traditional methods for the investigation of carbonium ions, it became necessary to seek a new approach. Such an approach, consisting in the study by the $^{13}C\{^1H\}$ and $^{13}C\{^1H, ^{57}Fe\}$ methods of organoiron compounds enriched in the $^{57}$Fe isotope (natural abundance 2.2%, nuclear spin 1/2), has been used in an investigation carried out at the Institute of Organoelemental Compounds of the USSR Academy of Sciences.[59,60] It was found that the $^{13}$C–$^{57}$Fe SSIC for ferrocene derivatives is relatively insensitive to the nature of the substituent and usually occurs in the range 4.2–5.2 Hz; the signal of the exocyclic $C_\alpha$ carbon atom in the $^{13}C\{^1H\}$ NMR spectrum is manifested by a narrow singlet.[59,61]

In contrast to ferrocene derivatives, the $^{13}$C–$^{57}$Fe SSIC for α-ferrocenyl carbonium ions are clearly not the same for different carbon atoms, being greatly reduced for C(3,4), while the signal of the $C_\alpha$ atom is either broadened or (when the resolution is sufficiently good) is observed as a doublet with a $^{13}C_\alpha$–$^{57}$Fe constant up to 2.7 Hz.[59,60]

The assignment of the observed broadening (splitting) of the signal of the $^{13}C_\alpha$ atom to interaction via only one bond ($^{13}C_\alpha$–$^{57}$Fe) and not via two bonds [$^{13}C_\alpha$–C(1)–$^{57}$Fe] has been justified[60] on the basis of the $^{13}$C–$^{57}$Fe SSIC obtained for $^{57}$Fe complexes with a wide variety of hydrocarbon ligands.

The broadening (splitting) of the $^{13}C_\alpha$ signal in the spectra of α-ferrocenylcarbonium ions is accompanied by a decrease of the $^{13}$C(3,4)–$^{57}$Fe SSIC, which suggests that the "non-bonding" hybrid *d* orbitals of iron undergo a rehybridisation, which promotes the Fe–$C_\alpha$ interaction.

The data on the shielding of $^{57}$Fe in the α-ferrocenylcarbonium ions $[FcCH_2]^\oplus$ (XXI) and $[FcCHCH_3]^\oplus$ (XXII) published in 1978 [59] confirmed this hypothesis. It has been

#The term "coordination shift" denotes the upfield shift of the NMR signals of the hydrocarbon ligand on coordination to the transition metal.

shown beforehand that the $^{57}$Fe chemical shift for ferrocenes is very sensitive to the nature of the substituent, electron-accepting substituents of the *-R* type leading to a marked deshielding of iron. Thus the $\delta(^{57}Fe)$ are 215.5 and 425.6 p.p.m. for acetyl- and 1,1'-diacetyl-ferrocenes respectively (relative to ferrocene as the standard).[59]

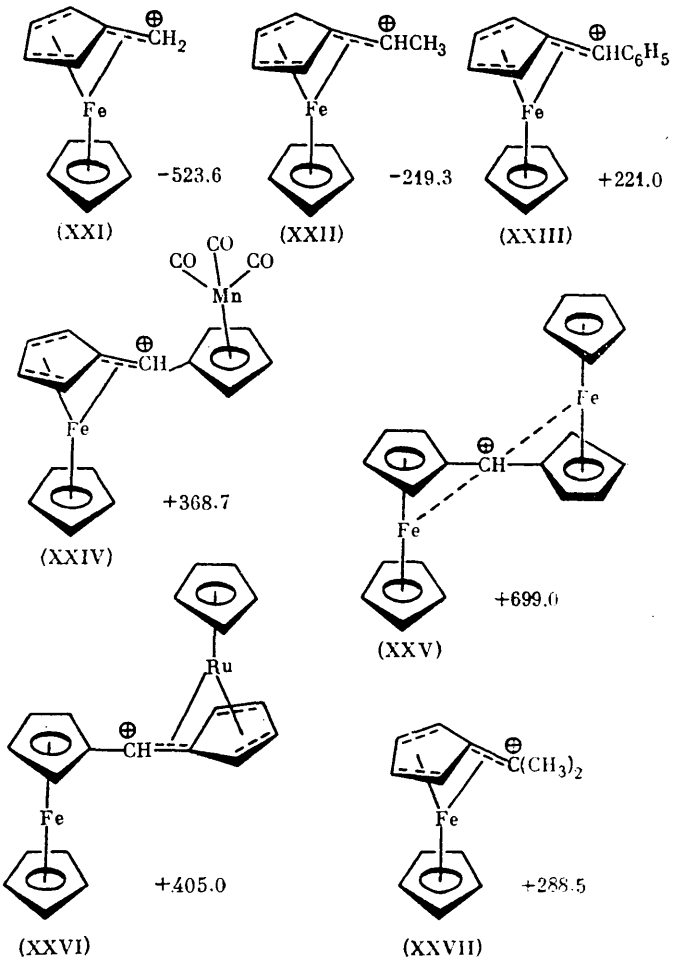



**Figure 1.** The $^{57}$Fe NMR chemical shifts (p.p.m.) of α-metallocenylcarbonium ions.[60]

However, despite the "electron-accepting" character of the substituent, the $^{57}$Fe signals of the carbonium ions (XXI) and (XXII) are observed in strong fields—at -523.6 and -219.3 p.p.m. respectively. The conclusion that the *d* orbitals are rehybridised in α-ferrocenylcarbonium ions has been supported by the following observations. The shift of the iron signal to a very strong field (-1098.8 p.p.m.) has also bee noted[61] for the protonated ferrocene $[HFe(C_5H_5)_2]^{\oplus}$, where the above rehybridisation is known to take place.[62,63] In addition an upfield shift has been observed also for those "uncharged" ferrocenophanes in which the rehybridisation of the "non-bonding" *d* orbitals is induced by the breakdown of the parallel arrangement of the rings as a consequence of the inadequate lengths of the hydrocarbon bridge.

It has been found that the $^{57}$Fe NMR signal undergoes consecutive upfield shifts with increase of the degree of deviation of the cyclopentadienyl rings of ferrocene from the parallel arrangement: the $\delta(^{57}Fe)$ chemical shifts for 1,1'-diethylferrocene, [4]ferrocenophane, and [3]ferrocenophane are +72.5, -56.5, and -272.5 p.p.m. respectively. In ferrocene derivatives containing a heteroannular bridge made up of three or four carbon atoms, the five-membered rings are known to deviate from the parallel arrangement by approximately 9° and approximately 4° respectively as a consequence of the tightening (in the former case) and expanding (pushing apart) (in the latter case) effects respctively. Thus the $^{57}$Fe signal of [3]ferrocenophane has undergone an upfield shift of approximately 350 p.p.m. compared with 1,1'-diethylferrocene containing parallel ligands.[60,64]

The study of the carbonium ions (XXI)–(XXVII) showed that their $^{57}$Fe chemical shifts cover a range of 1200 p.p.m. and constitute a sensitive measure of the direct involvement of the iron atom in the stabilisation of the carbonium ion centre (Fig.1). The relative shielding of the $^{57}$Fe nucleus in carbonium ions is determined by the sum of two opposed effects: the rehybridisation of the "non-bonding" *d* orbitals of iron promotes shielding, while the electron-accepting influence of the substituent promotes the deshielding of the $^{57}$Fe nucleus.

Thus the $^{57}$Fe chemical shifts for the series (XXI)–(XXVI) undergoes a consecutive [with the exception of the complex (XXV)] downfield displacement with increasing ability of the substituent R to delocalise the positive charge in the carbonium ions $[FcFHR]^{\oplus}$. The explanation is that, with increase in the ability of the group R to delocalise the charge, the contribution of the direct involvement of the metal to the stabilisation (i.e. the factor promoting the rehybridisation of its *d* orbitals, the $^{57}$Fe shielding factor) diminishes.[60,65]

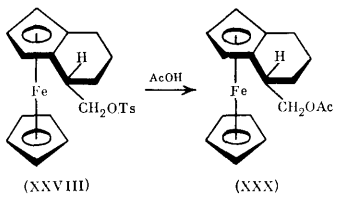
In the symmetrical complex $[(Fc)_2CH]^{\oplus}$(XXV) both ferrocenyl units make equal contributions to the delocalisation of the charge and the orbitals of each of the iron atoms are therefore less rehybridised [compared, for example, with the complex (XXIV)]; there is a simultaneous increase of the fraction of the charge delocalised via the system of carbon–carbon bonds of the cyclopentadienyl ligands. As a result, the complex (XXV) exhibits the most marked "carbenium ion" character among all the complexes (XXI)–(XXVII) investigated, which explains the marked deshielding of the iron nucleus in it (+699.0 p.p.m.). Data on the shielding of the $C_\alpha$ nuclei in the dinuclear complexes (XXIV), (XXV), and (XXVI) (122.4, 147.2, and 116.9 p.p.m. respectively) also agree with this finding.[60,65]

On the basis of the $^{13}C-^{57}Fe$ SSIC data for the shielding of the $^{57}$Fe nucleus in the cationic complexes (XXI)–(XXVII), one may assume that the strongest $Fe-C_\alpha$ bond obtains in the primary carbonium ion (XXI), although in this case too the strength of the $Fe-C_\alpha$ bond should be smaller than that of the bond with the carbon atoms of the five-membered ring. The greatest $^{13}C_\alpha-^{57}Fe$ shielding, amounting to 2.7 Hz, has been noted for the [3]ferrocenophan-7-yl cation,[60] which may be accounted for by the distortion of the fulvene ligand as a consequence of the additional tightening influence of the heteroannular bridge. The minimum $Fe-C_\alpha$ interaction evidently takes place in $[(Fc)_2CH]^{\oplus}$, whereas the results obtained indicate the occurrence of the $Fe-C_\alpha$ interaction in the tertiary carbonium ion $[FcC(CH_3)_2]^{\oplus}$[in contrast to the claim based on the Mössbauer spectra of this complex:[41] being highly sensitive, $^{57}$Fe NMR spectroscopy should indicate the occurrence of a weak $Fe-C_\alpha$ interaction in those cases where Mössbauer spectroscopy fails to record a change in the ligand environment of the metal on passing from the tertiary carbinol to the ion (XXVII)].

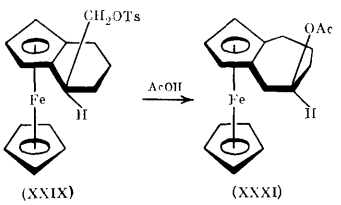
### 8. β-Ferrocenylcarbonium Ions

In view of the unusually high stability of α-ferrocenylcarbonium ions, it was of interest to discover how the ferrocenyl group influences the stabilisation of the carbonium centre in the β-position relative to it.

It has been observed[66] that *endo*-α-tosyloxymethyl-1,2-tetramethyleneferrocene (XXVIII) undergoes acetolysis 2780 times faster than its *exo*-isomer (XXIX). The corresponding acetate (XXX) is then formed from the *endo*-isomer, while the *exo*-isomer gives rise to the rearrangement product (XXXI), with a seven-membered ring:



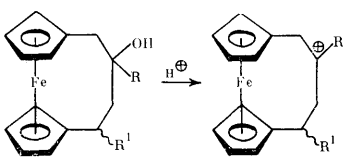

(XXVIII) (XXX)




(XXIX) (XXXI)

The difference between the rates of solvolysis of the complexes (XXVIII) and (XXIX) and also between the structures of the resulting products can be accounted for by the effective involvement of interannular electrons (in essence, the electrons of the iron atom) in the stabilisation of the β-ferrocenylcarbonium ion. The retention of configuration in the solvolysis of the optically active 1-ferrocenyl-2-propyl tosylate is consistent with the involvement of iron.[67]

The stability of β-ferrocenylcarbonium ions has been demonstrated in a $^1$H NMR study of the cationic complexes (XXXIII) generated from carbinols of the [4]ferrocenophane series (XXXII):[68–70]




(XXXII) (XXXIII)

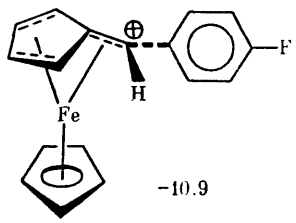
The effect of conjugation with the metallocenyl group is ruled out in the carbonium ions (XXXIII) where the electron-deficient centre is separated from the ferrocenyl group by the methylene unit. It is therefore natural to suppose that the stabilisation is achieved by the direct involvement of the iron atom.[69] The comparatively strong field of the C(7) hydrogen atom signal in complexes (XXXIII) (5.36–5.55 p.p.m.) agrees with this assumption.

## III. RELATED COMPLEX CARBONIUM IONS

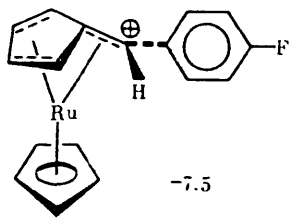
This Section does not deal with heteroatomic systems (for example, those generated by the protonation of acylferrocenes). These were partly considered in a previous review.[5] The presence of a heteroatom next to the carbonium ion centre can significantly reduce the role of the metallocenyl group in its stabilisation. Although these systems have been considered as models of α-ferrocenylcarbonium ions, this study has made little contribution towards the elucidation of the role of the transition metal atom in stabilisation.

### 1. Ruthenocenyl- and Osmocenyl-carbonium Ions

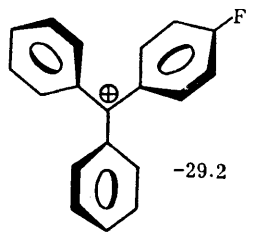
The rates of the $S_N1$ acetolysis of α-acetoxyethylmetallocenes[7] and of the non-catalysed addition of acetic acid to vinylmetallocenes[9] indicate an increase of carbonium ion stability in the sequence $[FcCHCH_3]^{\oplus} < [RucCHCH_3]^{\oplus} < [OscCHCH_3]^{\oplus}$ (where Ruc and Osc denote ruthenocenyl and osmocenyl). This stability series can be accounted for by the improvement of the overlap of the metal atom orbitals and the π orbitals of the fulvene ligand as the volume and polarisability of the valence shell of the metal increase.[2,3,7,71] The $pK_{R^+}$ for $[RucCHCH_3]^{\oplus}$ and $[FcCHCH_3]^{\oplus}$ are 1.20 and −0.65 respectively.[71]



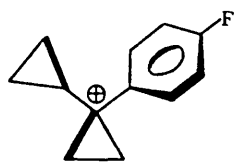

(XXXIV)




(XXXV)




(XXXVI)




(XXXVII)

Figure 2. The $^{19}$F NMR chemical shifts (p.p.m.) of the p-fluorophenyl-substituted carbonium ions.[75,76]

It has been shown for the optically active carbonium ions $[RucCHCH_3]^{\oplus}$ that the torsional barrier is so high that racemisation does not take place even when the solution in $CF_3COOH$ is heated at 70 °C for several days.[48]

The signals of the protons at $C_\alpha$ in the $^1$H NMR spectra of the carbonium ions $[McCHCHC(CH_3)_2]^{\oplus}$ (Mc = Fc, Ruc, Osc) as well as $[McCHCH_3]^{\oplus}$ (Mc = Fe or Ruc) undergo successive upfield shifts, which can be accounted for by the decrease of the positive charge on the $C_\alpha$ atom in the isostructural series of metallocenylcarbonium ions.[54,72]

According to $^{13}$C NMR data, the positive charge in the complex $[FeCHRuc]^{\oplus}$ (XXVI) is largely delocalised over the ruthenocenyl unit. The spectrum exhibits a temperature dependence due to the rotation about the Fe–$C_\alpha$ bond.[60,65] It is of interest to compare these results with data concerning the electronic influence of the corresponding metallocenyl

groups. It has been shown that, according to $^{19}F$ NMR data for the complexes *m*- and *p*-$Fc_6H_4Mc$, characterising the influence of the metallocenyl groups in the ground state of the uncharged substrates, the metallocenyl groups Fc, Ruc, and Osc show insignificant differences in their electronic influences, which are close to those of the alkyl substituents in the benzene ring.[73] Furthermore, estimation of the effective charges in metallocenes (also on the basis of the shielding of the $^{19}F$ nucleus) yielded the following values for the cyclopentadienyl ligand in ferrocene, ruthenocene, and osmocene: −0.26, −0.25, and −0.25 a.u. respectively.[74] In the light of these data, it is reasonable to postulate that the results obtained for the complex $[FcCHRuc]^{\oplus}$ agree with the direct involvement of the ruthenium atom in stabilisation.[60]

The $^{19}F$ NMR signals of the carbonium ions (XXXIV) and (XXXV) are observed at −10.9 and −7.5 p.p.m. respectively (in a weak field relative to fluorobenzene). Thus the ruthenocenyl group is more effective in delocalising the charge than the ferrocenyl group[75] (Fig.2).

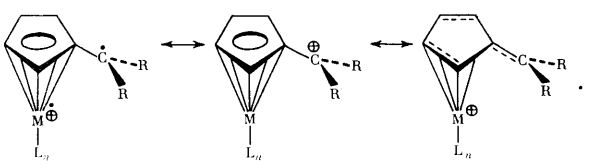
Comparison of the shielding of $^{19}F$ in the complexes (XXXIV) and (XXXV) and in the carbenium ions (XXXVI) and (XXXVII) [76] demonstrates to what extent the metallocenyl groups are superior to the phenyl and cyclopropyl groups as regards the delocalisation of the positive charge. The similarity of the $^{19}F$ chemical shifts for the complexes (XXXIV) and (XXXV) to those for *p*-fluoronitrobenzene and *p*-cyanofluorobenzene (−11.1 and −9.2 p.p.m. respectively) has also been noted.[75] Hence it follows that the treatment of the $C_\alpha$ atom as a "carbonium ion" centre is to a considerable extent arbitrary.

## 2. Cymantrenylcarbonium Ions

The cymantrenyl group is less effective in stabilising the cationic centre than the ferrocenyl group, but it is superior to the phenyl group in this respect.[77–80]

The substitution of the CO ligands by phosphine ligands increases the stabilisation of the corresponding ions, as might have been expected on the basis of the donor–acceptor properties of CO and $PR_3$ groups.[81]

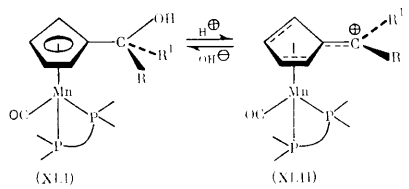
The similarity of the ultraviolet[80] and $^1H$ NMR [80,82,83] spectra of α-cymantrenyl- and α-ferrocenyl-carbonium ions suggested the similarity of the mechanisms of their stabilisation. A distinctive feature of the $^{13}C$ NMR spectra of cymantrenylcarbonium ions is that the signal due to the C(1) atom exhibits the greatest degree of shielding. According to Loim et al.,[84] the structure of α-metallocenyl carbonium ions (including cymantrenyl ions) may be described by the resonance of the structures (XXXVIII), (XXXIX), and (XL), in which the exocyclic bond is inclinded in the direction of the metal atom.



(XXXVIII) (singlet state) (XXXIX) (XL)

The contribution of each structure depends on the nature of the metal, its lipand environment, and the substituents at the $C_\alpha$ atom. With increase of the number of electron-donating substituents at this atom the stabilisation due to the $M-C_\alpha$ interaction diminishes owing to steric hindrance. The "approach of the cationic centre" to the plane of the five-membered ring diminishes the contribution of the structure (XXXVIII) with the direct involvement of the metal atom and correspondingly increases the contribution of the structures (XXXIX) and (XL). Overall, these considerations agree with those presented previously[37] for α-ferrocenylcarbonium ions and are not open to objection. However, it has not been explained why the exocyclic bond in the structures (XXXIX) and (XL), where a direct involvement of the metal atom in stabilisation is not implied, should nevertheless be inclined towards the metal atom.

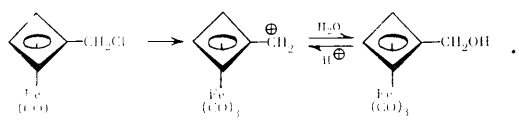
Two $^{31}P$ signals are sometimes observed when the cationic complexes (XLII), generated from the diphosphine derivatives of the cymantrenyl carbinols (XLI), are investigated by $^{31}P$ NMR, which is explained by hindrance to free rotation of the $Mn(CO)P_2$ group about the metal–ring axis, possibly owing to the inclination of the exocyclic bond.[85]



(XLI) (XLII)

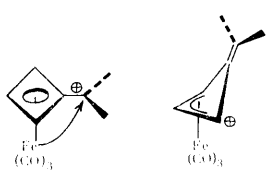
## 3. Tricarbonyliron(η-cyclobutadienyl)carbonium Ions

It has been shown that tricarbonyliron(α-chloromethylcyclobutadiene) (XLIII) undergoes rapid solvolysis in water or methanol, giving rise to the carbinol (XLV) or the corresponding methyl ether. These reactions have been explained by the intermediate involvement of the stable carbonium ion (XLIV). The latter has been isolated in the form of the $SbCl_6^-$ salt on treatment of the complex (XLIII) with antimony pentachloride.



(XLIII) (XLIV) (XLV)

In order to account for the pronounced shielding of the exocyclic protons in the $^1H$ NMR spectrum of the carbonium ion (XLIV) (signals at δ = 6.68, 5.91, and 5.09 p.p.m. with the relative intensities 1:2:2) and also of the secondary carbonium ion generated from tricarbonyliron(η-α-hydroxyethylcyclo butadiene), the structures (XLVI) and (XLVII) were examined and preference was given to the π-allyl structure (XLVII).[13]

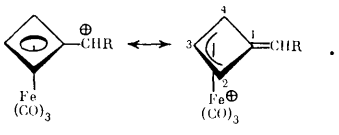


(XLVI) (XLVII)

On the basis of the results of X-ray diffraction analysis of the tetrafluoroborate salt of the cation $\{[(OC)_3Fe(\eta\text{-}C_4H_3)]_2.CC_6H_5\}$, the authors later concluded[14] that the main contribution to stabilisation comes from the interaction between the occupied orbitals of the metal atom and the four carbon

atoms of the cyclobutadiene ring with subsequent electron transfer to the electron-deficient centre via π,π interaction.

In the study of the cationic complexes $[(OC)_3Fe(\eta\text{-}C_4H_3).CHR]^{\oplus}$(R = H, $CH_3$, or $C_6H_5$) by $^{13}C$ NMR, it was noted[86] that $\Delta\delta(^{13}C_\alpha)$ is comparatively small for the transition from the carbinol to the carbonium ion (in contrast to organic systems). Furthermore, an appreciable downfield shift of the signal of the C(3) carbon atom (42–46 p.p.m.), compared with 3–13 p.p.m. for the C(2) and C(4) atoms, has been observed. These data can be accounted for in terms of hyperconjugation with participation of the metal–carbon bond.[11,87] It is believed[87] that the hyperconjugation effect weakens the bond between the metal and the C(1) atom, which increases the contribution of the π-allyl structure to the resonance hybrid (XLVIII)↔(XLIX):



(XLVIII) (XLIX)

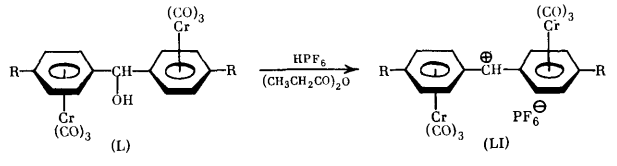
However, the above spectroscopic features may be a result of the rehybridisation of the iron atom, which ensures the Fe–$C_\alpha$ direct interaction.

## 4. Benchrotrenylcarbonium Ions

The study of tricarbonylarenechromium-substituted systems has the advantage that it makes possible a direct comparison with the corresponding non-coordinated arenes. The solvolysis of $(OC)_3Cr(\eta\text{-}C_6H_5CH_2Cl)$ is approximately $10^5$ times faster than that of benzyl chloride, while the solvolysis of η-chlorodiphenylmethanechromium tricarbonyl is approximately $10^3$ times faster than that of diphenylmethyl chloride.[88] A slight increase (only by a factor of 28) of the rate of solvolysis of α-chlorocumene on coordination to the $Cr(CO)_3$ group can be explained by the influence of steric factors.[89]

Data obtained from measurements of the $pK_{R^+}$ for benchrotrenylcarbonium ions also indicate the ability of the $Cr(CO)_3$ group to delocalise the charge.[90,91]

The attempts to obtain stable salts of carbonium ions from $(OC)_3Cr(\eta\text{-}C_6H_5CH_2X)$ (X = Cl or $CH_2OH$) were unsuccessful.[88] The stable $PF_6^-$ salts of the carbonium ions (LI, R = H or $CH_3$) have been synthesised only from the dimetallic carbinols (L):[92]



(L) (LI)

The 1-(tricarbonyl-*p*-tolylchromium)ethyl and bis(tricarbonyl-*p*-tolylchromium)methyl cations, generated from the corresponding carbinols in $HSO_3F$ at −50 °C, have been identified by $^1H$ NMR.[93] $^{13}C$ NMR data for the same carbonium ions were published later.[92,94] Although the results presented did not enable the authors[94] to make a choice between the resonance-stabilised structure and the structure involving the direct participation of the metal atom, preference was given to the latter.

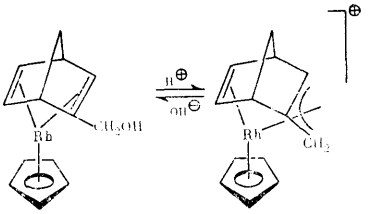
In a study of the $^{13}C$ NMR spectrum of the tricarbonylcumenylchromium cation (LII), it was noted[95] that, whereas the *ortho*- and *para*-carbon atoms in benchrotrenes and non-coordinated monosubstituted benzenes are usually more sensitive to the influence of substituents than the *meta*-carbon atoms, in the carbonium ion (LII) the opposite situation is observed: the *meta*-carbon atoms proved to be the most deshielded. On this basis, the authors regard the direct involvement of the metal atom and delocalisation via the overlap of the π,π type as unlikely; a significant role of the σ,π conjugation is also rejected (the appearance of a signal due to $C_i$ in a very weak field would be expected in such a case). The authors merely state that the charge is delocalised over the $Cr(CO)_3$ group, although the mechanism of the delocalisation remains obscure.

According to a calculation by the LCAO-MO SCF method, the stability of the $[(OC)_3Cr(\eta\text{-}C_6H_5CH_2)]^{\oplus}$ ion is the result of the supply of the electrons from the $d_{x^2-y^2}$ orbital of chromium to the non-bonding π orbital of the benzyl ligand.[96] The mechanism corresponds to the direct participation of the metal atom but not via the formation of a specific Cr–$C_\alpha$ bond but as a result of the interaction with the π-benzyl ligand as a whole. The angle of inclination of the exocyclic bond towards the metal is 40°.

## 5. Carbonium Ions Stabilised by Olefins and Dienes Bound in Complexes

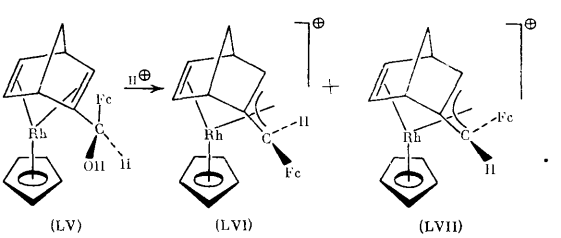
In the chemistry of transition metal π-complexes, it is well known that the generation of a carbonium ion centre next to a coordinated π-olefinic linkage transforms the olefin complex into a cationic π-allyl complex.

The stereochemistry of similar reactions and the influence of the character of the substituents at the exocyclic carbinol carbon atom has been investigated in detail in relation to norbornadiene carbinols.[97–100] Treatment of the carbinol (LIII) with acid results in the formation of the cationic complex (LIV) in which the bicyclic ligand is linked to the metal via π-ethylenic and π-allyl bonds.[98] The structure of this complex, proposed on the basis of $^1H$ and $^{13}C$ $^1H$ NMR data, has been confirmed by X-ray diffraction.[97]



(LIII) (LIV)

It has been shown for the diastereoisomeric 2-(α-hydroxyethyl)norbornadienecyclopentadienylrhodium complexes with the ψ-*exo*- and ψ-*endo*-configurations of the OH group that the elimination of the hydroxy-group is highly stereospecific and leads to the *syn*- and *anti*-allyl cationic complexes respectively.[97–100] The stereospecificity is retained also in the reaction of the phenyl-substituted ψ-*endo*-carbinol, while a mixture of the *syn*- and *anti*-isometric complexes (LVI) and (LVII) is obtained from the ferrocenyl-substituted ψ-*endo*-carbinol (LV) in proportions of 4:1, i.e. the complex having the expected configuration is obtained in a lower yield:

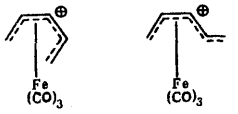


(LV) (LVI) (LVII)

The breakdown of stereospecificity in the reaction involving the elimination of the hydroxy-group from the carbinol (LV) can be accounted for by the competition between the iron and rhodium atoms in the stabilisation of the carbonium ion centre in the transition state of the reaction.[97]

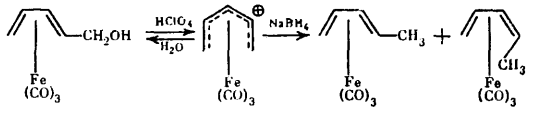
Considerable efforts have been devoted to the elucidation of the structure and mechanism of the stabilisation of the carbonium ions generated from dieneiron tricarbonyl complexes.[101]

The cationic pentadienyl complexes can exist in both the *cis*-form (LVIII) and the *trans*-form (LIX):



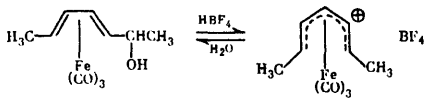
(LVIII) (LIX)

Although the formation of complexes of type (LIX) has been postulated in many reactions, for a long time they could not be detected owing to the ease of their rearrangement to the more stable *cis*-isomers (LVIII). Thus treatment of the complex (LX) with perchloric acid yielded the salt of the *cis*-cation (LVIII):[102]



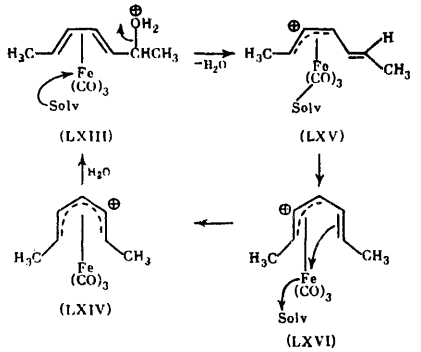
(LX) (LVIII) (LXI) (LXII)

The carbonium ion (LVIII) reacts with water, regenerating the *trans*-pentadienecarbinol (LX).[102] Such stereoselectivity does not always obtain in the reaction of the cation (LVIII) with nucleophiles. Treatment of salts of the carbonium ion (LVIII) with sodium tetrahydroborate yielded a mixture of the isomers (LXI) and (LXII) in proportions of 1:4.[102] The tricarbonyl-*syn*,*syn*-1,5-dimethylpentadienyliron cation (LXIV) has been regenerated from the diastereoisomeric carbinols (LXIII) by treatment with acids. Its hydrolysis is stereospecific and involves the formation of one of the isomeric carbinols:



(LXIII) (LXIV)

The following mechanism has been postulated to account for the stereochemistry of these reactions:[102]



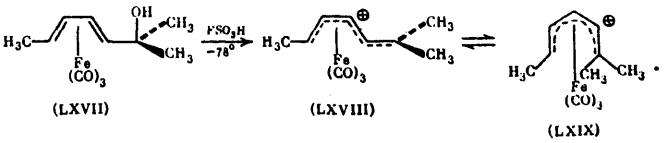
(LXIII) (LXV) (LXIV) (LXVI)

In the first stage both diastereoisomeric carbinols are converted (albeit at different rates) to the hydrated vinylallyl complex (LXV). Rotation about the single bond in compound (LXV) affords compound (LXVI) and subsequent displacement of the solvent molecule and coordination to the vinyl bond leads to compound (LXIV). The *exo*-attack on the cation (LXIV) by the $OH^{\ominus}$ion regenerates one of the carbinols (LXIII).

The study of the solvolysis of the 3,5-dinitrobenzoates of the diastereoisomeric carbinols of the butadieneiron tricarbonyl series showed that the solvolysis proceeds via the $S_N1$ mechanism with retention of configuration.[103] The study of the reaction products by spectroscopic methods indicates the retention of the initial carbon skeleton in the carbinols formed: thus the intermediate species in these reactions are tricarbonyl-*trans*-η-pentadienyliron cations.

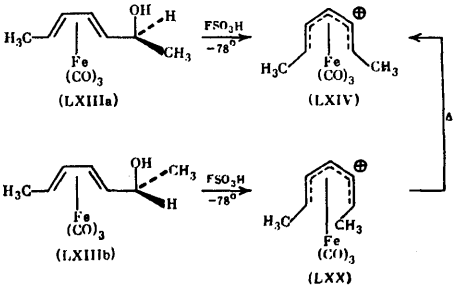
According to the authors,[103] the solvolytic data agree both with the direct nucleophilic involvement of the metal atom and with the hyperconjugation of the metal–carbon bond.

The direct detection of the *trans*-pentadienyl cations by $^1$H NMR was achieved after many attempts[104–107] by employing appropriately substituted dienol complexes.[105,106] After dissolving the carbinol (LXVII) in cooled fluorosulphonic acid, the formation of the *trans*-cation (LXVIII), in equilibrium with its *cis*-isomer (LXIX), was observed:[105]



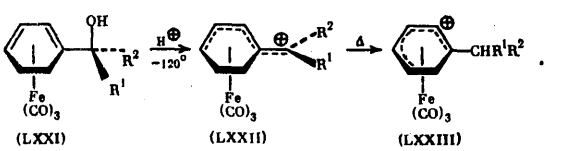
(LXVII) (LXVIII) (LXIX)

In the same study[105] it was shown that, when the reaction of the diastereoisomeric carbinols (LXIII) is carried out at a low temperature, a stereospecific conversion into the *cis*-ions (LXIV) and (LXX) takes place [in contrast to the data of Mahler and Pettit[102] who isolated only the cation (LXIV) from both carbinols]. The *trans*-cations could not be detected in this case. It was therefore assumed that the structure of the carbonium ions generated is determined not only by steric but also by electronic factors.[105]



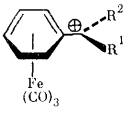
(LXIIIa) (LXIV) (LXIIIb) (LXX)

Cyclic *trans*-cations (LXXII), generated at −120 °C in solution in the $FSO_3H$–$SO_2ClF$ mixture from the carbinols (LXXI), have been detected by $^1$H NMR.[108] On raising the temperature of the solution, the complexes (LXXII) rearrange to the more stable cyclohexadienyl cations (LXXIII):



(LXXI) (LXXII) (LXXIII)

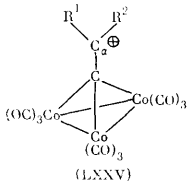
The rate of the rearrangement of the secondary ion (LXXII, $R^1 = H$, $R^2 = CH_3$) is much higher than that of the tertiary ion (LXXII, $R^1 = R^2 = CH_3$). On this basis, it has been suggested that the positive charge is localised on the exocyclic carbon atom. The authors therefore believe that the tetrahapto-structure (LXXIV) makes an important contribution to the overall structure of the complex and the stability of these cationic complexes should be a result of the delocalisation of the charge via a conjugation mechanism.[108]



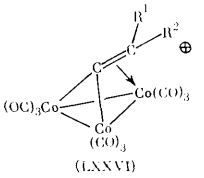
(LXXIV)

## 6. Carbonium Ions Stabilised by the $Co_3(CO)_9C$ and $Os_3H_3(CO)_9C$ Clusters

Seyferth and co-workers[109] investigated thoroughly the cationic complexes stabilised by the nonacarbonyltricobalt-methinyl group. The cationic complexes $[Co_3(CO)_9CCR^1R^2]^{\oplus}$ were isolated in the form of stable salts with the $PF_6^{\ominus}$ anion. The structure of the carbenium ion (LXXV) with the $Co_3C-C_\alpha$ bond directed at right angles to the plane of the $Co_3$ triangle was postulated for them. The high stability of the cationic complex was accounted for by the $\sigma,\pi$ conjugation mechanism.[110–112]

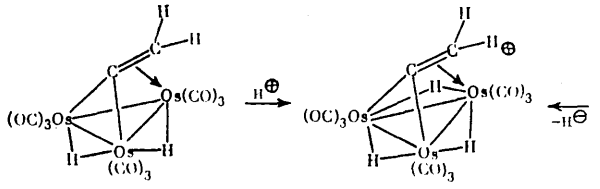


(LXXV)

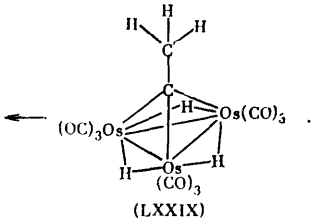


(LXXVI)

An alternative structure (LXXVI) with an inclined $\mu_3$-$\eta^2$-hydrocarbon ligand has been suggested on the basis of $^1H$ NMR data for the related osmium complex $[Os_3H_3(CO)_{10}\cdot(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)^{\oplus}]$ (LXXVII), generated by protonating the dihydride complex (LXXVIII) or by eliminating a hydride ion from the methyl group of the complex (LXXIX).[113]



(LXXVIII) (LXXVII)



(LXXIX)

The spectrum of the complex (LXXVII) in the $CF_3COOH$–$CDCl_3$ mixture at −10 °C contains two hydride signals with relative intensities in proportions of 2 : 1 at −18.36 and −20.58 p.p.m. When the solution is heated, the hydride signals are broadened and merge into a singlet at 70 °C. It has been suggested[113] that the temperature dependence of the spectrum can be a consequence of either the migration of the hydride ligands relative to the $Os_3$ triangle or of the formation of a carbenium ion at an elevated temperature, as in the case of the complex (LXXV). Yet another explanation of the stereochemical non-rigidity of the complex (LXXVII) in relation to its cobalt analogue has been proposed. It consists of the rearrangement of the $\mu_3$-$\eta^2$-hydrocarbon ligand. This process has been examined theoretically by Schilling and Hoffmann,[114,115] who state that the inclined structure (LXXVI) corresponds to the ground state of the complex $[Co_3(CO)_9CCH_2]^{\oplus}$. The experimental data obtained in a $^{13}C$ NMR study of the complex $[Co_3(CO)_9CCHCH(CH_3)_2]^{\oplus}$ are consistent with this finding. The signals of the methyl carbon atoms are anisochronic at −65 °C, in conformity with the structure (LXXVI), where they are diastereotopic. With increase of temperature, the signals of the methyl carbon atoms in the isopropyl substituent coalesce, possibly as a consequence of the correlated rotation about the $Co_3(CO)_9$–C and C–$CHCH(CH_3)_2$ axes. However, spectroscopic data do not rule out a non-correlated rotation [i.e. the rotation of the $CHCH(CH_3)_2$ fragment without the simultaneous rotation of the $Co_3(CO)_9$ unit] or the formation of the carbenium ion structure (LXXV) at elevated temperatures.

The observation of satellites due to the $^{187}Os-^1H$ spin–spin interaction (natural abundance of the $^{187}Os$ isotope 1.64%, nuclear spin 1/2) in the $^1H$ NMR spectra of the cationic complexes $[Os_3H_3(CO)_9CR^1R^2]^{\oplus}$ established that the temperature variation of the spectrum is due to the migration of the hydrocarbon and not the hydride ligands.[117,118] One hydride signal at $\delta$ = 19.63 p.p.m. has been observed in the $^1H$ NMR spectrum of the complex $[Os_3H_3(CO)_9C\overline{C(CH_2)_2CH_2}]^{\oplus}$ at 30 °C. Two pairs of satellites (with 28.8 and 32.0 Hz splittings) have been noted on either side of the signal. It has been demonstrated by the method of double homonuclear resonance that the $^{187}Os-^1H$ SSIC is 30.4 Hz and the double set of satellites in the spectrum is explained by the further splitting of the satellite signal as a consequence of the spin–spin interaction with the third hydrogen atom which is not linked to the $^{187}Os$ isotope. The $^{187}Os-^1H$ SSIC, amounting to 30.4 Hz, lies in the range 27–35 Hz characteristic of saturated osmium complexes with stereochemically rigid (bridging) hydride ligands.

## IV. CONCLUSION

Examination of the literature data presented above permits the conclusion that the structure of some of the cationic complexes and the role of the transition metal atom in their stabilisation have now been reliably established. This applies in the first place to the α-metallocenylcarbonium ions and also to cationic complexes of the type $[Co_3(CO)_9CCR_2]^{\oplus}$ and $[Os_3H_3(CO)_9CCR_2]^{\oplus}$. Although the available data for other related complexes are not quite so unambiguous, they are in overall agreement with the direct involvement of the metal atoms in the stabilisation of the carbonium ion centre.

One can therefore assume that the *ability (tendency) of the transition metal atom to enter into a direct interaction with the carbonium ion centre generated in the β-position relative to its is a general property of transition metal complexes.* Exceptions are possible in those cases where the need for the direct interaction with the metal atom does not arise because of the presence of heteroatomic substituents at the carbonium ion centre.

The validity of this generalisation can be confirmed by studying cationic complexes whose structure and the mechanism of the stabilisation of which have not yet been established. For example, stable complexes having the compositions $[(RC{\equiv}CCR^1R^2)Co_2(CO)_6][BF_4]$ [119,120] and $[(HC{\equiv}CCR^1.R^2)M_2(CO)_4(C_5H_5)_2][BF_4]$ (M = Mo or W) [121] and obtained from the corresponding complex ethynylcarbinols[121-123] are now known; they are usually regarded as carbenium ions. However, the spectroscopic characteristics and the set of available data for the related cationc complexes suggest that in these complexes too the metal atom interacts directly with the "carbonium ion centre".

In connection with the structure and the stabilisation mechanism mention should be made of the "redox tautomerism" of ferrocenylcarbonium ions.[124,125] It has been suggested[125] that ferrocenylcarbonium ions can readily undergo an intraionic oxidation-reduction reaction in which an electron is transferred from the metal atom to the "carbonium ion centre" $C_\alpha$ with formation of the ferricenium biradical cation. Calculation by the MO method[15] predicted that this type of reaction should be accompanied by a change in the geometry of the fulvene ligand—the latter should be planar in the triplet ferricenium cation.

Experiments with a spin trapping agent seemingly confirmed the hypothesis of the possible redox tautomerism,[125] but subsequently it was noted[126] that the formation of nitroxyradicals following the addition of nitrosobenzene to the ferrocenylcarbonium ion can also proceed via other pathways not involving the biradical redox tautomer.

Nevertheless one can assume that, in the presence of a suitable ligand environment, it is possible to achieve an intraionic oxidation-reduction reaction of the metallocenylcarbonium ion. Studies on these lines are being prosecuted by Rybinskaya and co-workers.[127]

The general assessment of the long controversy concerning the structure and mechanism of the stabilisation of α-ferrocenylcarbonium ions is that it has been extremely useful. Numerous studies of the factors influencing the stability of organic carbonium ions (the involvement of neighbouring groups in solvolytic reactions, the "problem of non-classical ions",[128] the σ- and π-donation of electron density by heteroatomic substituents,[129] the possibility of the donation of π electrons by the electron-accepting substituents CN, CHO, $CF_3$, and $\overset{\oplus}{N}H_3$,[130] and other problems) are being continued. It is therefore evident that the understanding of the mechanism of the delocalisation of the positive charge in the α-ferrocenylcarbonium ions and related cationic complexes extends our overall ideas about carbonium ions—these most important species in organic chemistry.

Furthermore, the elucidation of the way in which the transition metal atom influences the delocalisation of the positive charge (reactivity) of the organic ligand bound to it is now particularly timely, an increasing number of cationic complexes finding applications in the synthesis of organic compounds.[131,132]

In conclusion, we have to consider the names of the cationic complexes $[FcCR^1R^2]^{\oplus}$. The following notation has been adopted for them in the literature: α-ferrocenylcarbenium ion, α-ferrocenylcarbonium ion, and fulvenecyclopentadienyliron cation.

According to $^{57}Fe$ NMR and X-ray diffraction data, the exocyclic $C_\alpha$ atom in these complexes usually interacts with the metal atom. Consequently it is not tervalent and the term "carbenium ion" is not applicable to these systems.

Judging from the $^{19}F$ NMR chemical shifts, the fraction of the positive charge localised on the $C_\alpha$ atom in the complex $[FcCHC_6H_4F\text{-}p]^{\oplus}$ is so small that the term "fulvenecyclopentadienyliron cation" must be recognised as adequately justified, being particularly valid for the complex $[FcCH_2]^{\oplus}$. However, the $^{13}C$ and $^{57}Fe$ NMR studies of the complex enriched in the $^{57}Fe$ isotope have shown that the $Fe{-}C_\alpha$ interaction weakens with increasing capacity of the groups $R^1$ and $R^2$ to delocalise the charge and the fraction of the charge delocalised via the system of carbon–carbon bonds increases. In this case the term "α-ferrocenylcarbonium ion" appears more suitable. Although the latter term cannot be regarded as adequate, it has the advantage that it reflects the genesis of these complexes.

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# Dinuclear Metallocenes

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Data on the methods of synthesis and chemical reactions of bismetallocene complexes of Group IV-VI transition elements are analysed. Attention is concentrated on the determination of the general characteristics of the structure and reactions of dinuclear metallocenes and also on the analysis of the discrepancies frequently arising in studies of these compounds. The bibliography includes 117 references.

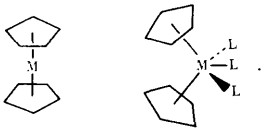
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## I. INTRODUCTION

Since the discovery of ferrocene and the synthesis of its closest analogues, the modern stage of the development of the organic chemistry of transition and non-transition elements has begun. The synthesis of new unusual structures has sharply stimulated research into the theory of the chemical bond, studies on the synthesis of a wide variety of skeletal structures, regardless of the elements constituting them, and a vigorous development of virtually all the physical research methods, for which these new compounds have been an extremely rewarding object of study.

Among the entire wide variety of transition metal complexes with organic ligands obtained at the present time, the carbonyl and biscyclopentadienyl compounds continue to retain their leading position. This is caused mainly by the strength of the binding of the ligands in these complexes to the transition metal atoms, which makes it possible to carry out a wide range of reactions of these complexes in most cases without risk of a complete and unpredictable rearrangement of the entire ligand sphere of the metal. The wide variety of the chemical properties and the high stability of the metallocene $(Cp_2M)$† analogues of ferrocene in terms of the Group and Period permitted the hypothesis, put forward in the early stage of these studies, that the sandwich structure (I) with a parallel arrangement of the Cp rings is universally applicable to the complexes of all transition metals.




(I) (II)

Numerous attempts have therefore been made to obtain such compounds for all transition metals. However, it was found that the synthesis of mononuclear homoligand metallocenes (I) is not easy for transition elements located at the beginning and end of the long Periods; this is manifested particularly strikingly in the second and third transition series. The phenomenon is caused by the inconsistency, as regards these elements, between the coordinating capacity of the Cp ligand and the coordination requirements of the metal atom and also by the very markedly unfavourable character of the filling of the bonding and antibonding orbitals of the metal–ring bond. This results in a decrease of the overall metal–ring bond order, which facilitates the distortion of the sandwich and its conversion into wedge-shaped derivatives of the type $Cp_2ML_{1-3}$ or into the monocyclopentadienyl complexes $CpML_n$.

This review deals with compounds of the Group IV, V, and VI elements at the beginning of the large Periods. Such differentiation of the objects of study is natural and easily attainable, since the majority of the transition metals in these Groups form compounds having similar structures; in addition, the methods of synthesis (of the complexes) and the reactions undergone by these derivatives are also similar. The very first and most general structural feature which it is appropriate to identify already at this stage is the tendency of these elements to form heteroligand wedge-shaped derivatives $Cp_2M(L)_{1-3}$ (II) in which the additional groups L are located in the bisector plane of the wedge-shaped sandwich.

Among all the nine elements of the above Groups, stable compounds, whose molecules consist of regular sandwiches of type (I), have been isolated only for vanadium and chromium (vanadocene and chromocene).[1,2] The relatively small size of the vanadium and chromium atoms enables the cyclopentadienyl ligands to exhaust to a large extent the coordinating capacity of the metal atoms in the regular sandwich structures, virtually isolating them from the possibility of attack by external reagents. Although the instances of the expansion of the coordination sphere of these elements above the formal hexacoordinate sphere in $Cp_2M$ are feasible and known,[1,2] nevertheless the $Cp_2V$ and $Cp_2Cr$ molecules are kinetically fairly inert in many reaction mixtures, which makes it possible to isolate these complexes as individual crystalline products. As regards the remaining seven elements (Ti, Zr, Hf, Nb, Ta, Mo, and W), the structure of their biscyclopentadienyl complexes proved to be much more complex and the problem has not been yet fully elucidated. None of the early mentions of the synthesis of monomeric metallocenes of these elements were subsequently confirmed. The history of the development of the research into titanocene, the representation of the formula of which by $(C_5H_5)_2Ti$ can be encountered in the early communications by very many investigators together with claims that all operations have been carried out with an individual compound having precisely this structure, is most interesting and instructive.

Only in the very recent years has direct experimental confirmation been obtained for the existence of the extremely

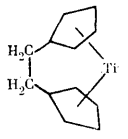
†Here and henceforth the symbol Cp has been adopted for the $\eta^5$-cyclopentadienyl ligand.

reactive mononuclear complexes of niobium ($Cp_2Nb$) [3] and molybdenum and tungsten ($Cp_2Mo$ and $Cp_2W$) [4] with structure (I) analogous to that of ferrocene, as well as the titanium compound $(Me_5C_5)_2Ti$. [5,6] However, the experimental details quoted in the above studies[3–6] show that there is virtually no hope of isolating pure crystalline specimens of these complexes, since at room temperature they undergo either rapid dimerisation (the Nb, Mo, and W complexes) or the sandwich structures isomerise (the Ti complex). We may predict with a considerable degree of confidence that in the case of the mononuclear metallocenes of other Group IV–VI elements the situation will be entirely analogous, i.e. that direct experimental confirmation of their existence also will be obtained in the next few years. On the other hand, the set of data available at present allows virtually no doubt as to the formation of mononuclear compounds of type (I) as intermediate species in various chemical reactions of derivatives of these elements.

A series of theoretical studies have been made on the stereochemical and electronic structures of mononuclear metallocenes as a function of the position of the central metal atom in the transition series; the complete list of references can be found in a series of communications.[7–10] Analysis of the variation of the energies of three frontier molecular orbitals (MO) of the sandwich systems as a function of the angle θ characterising the distortion of the metallocene fragments has led to the conclusion that the regular sandwich structure ($\theta = 180°$) and not the wedge-shaped sandwich is preferable for the monomeric homoligand species.



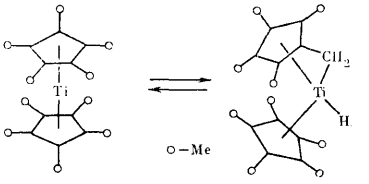

(III)




(IV)

The energies of these frontier MO, which are located in the bisector plane of the wedge-shaped sandwich and are predominantly the *d* orbitals (70–80%) of the metal, increase appreciably with decrease of θ. The energies of the deeper Cp–M bonding MO should also increase appreciably with decrease of θ. Consequently the distortion of the sandwiches requires a definite energy expenditure. The structures of all the known monomeric transition metal metallocenes, including the complexes $Cp_2Mo$, $Cp_2W$, and $Cp_2Nb$ which have been detected only at a low temperature, are consistent with this conclusion.

On the other hand, the mononuclear metallocenes of Group IV–VI elements should remain distinctly carbene-like (carbenoid) complexes, since the frontier MO (in the regular sandwich these are two degenerate $e_2$ orbitals and the $a_1$ orbital having a similar energy) are only partly filled by electrons. The carbenoid character of many metallocene derivatives of these elements has been confirmed chemically by the ease of oxidative addition and ligand addition reactions. In conformity with the Jahn–Teller theorem, a distortion of the regular sandwich structure may be expected only for the elements of the titanium subgroup, but this would not alter the carbenoid character of the molecules, while an increase of the accessibility of the metallic centre, which occurs because the angle θ ceases to be 180°, increases still further the likelihood of the formation of wedge-shaped derivatives having the composition $Cp_2MX_{1-2}$. Experimental data permitting at least approximate inferences about the stereochemical configuration of the mononuclear metallocenes in the titanium subgroup are at present lacking. The greatest hopes are with further studies of decamethyltitanocene,[5,6,11,12] whose existence as a homoligand complex has been demonstrated but only in equilibrium with the isomeric cyclopentadienylfulvenetitanium hydride compound:




The search for methods of synthesis of titanocenophane (IV) with a fairly short bridge is also promising. The first study[13] on these lines demonstrated that the reactions which proceed readily for unsubstituted titanocene derivatives and which proceed preferentially via the homoligand complex $(C_5H_5)_2Ti^{II}$ cannot be achieved for the complex with a bridging ligand. The first stage of the reaction, namely the reduction of titanium (IV) or titanium (III) to titanium (II) with formation of the complex (IV) as a kinetically independent species, is then unsuccessful.

The carbenoid character and coordination accessibility of the central metal atom to attack by external reagents are the main causes responsible for the vanishingly low stability of the homoligand monomeric metallocenes of type (I) formed by Group IV–VI metals. The complexes $Cp_2V$ and $Cp_2Cr$ (see above), containing metals with the smallest atomic radii, are an exception. However, these complexes too are highly reactive and are readily converted into the wedge-shaped structures $Cp_2ML_n$ and are unstable when acted upon by atmospheric oxygen and moisture. For all the remaining metals of these Groups, the complexes $Cp_2ML_n$ are virtually the only form of the compounds in which the metallocene fragment is present.

The spontaneous formation of dinuclear compounds in reactions where the formation of monomeric metallocenes of type (I) would be expected constitutes perhaps the most striking confirmation of the preferred formation of wedge-shaped structures where metal atoms are bound not only to the $\eta^5$-cyclopentadienyl ligands but also to other groups. The vast majority of bismetallocene structures obtained at the present time for the Group IV–VI elements are formed as a result of the insertion of one carbene-like metallocene fragment in the C–H bonds of the ligands of a second analogous fragment.

The first hypothesis that the metallocenes of Ti, Zr, Hf, Nb, Ta, Mo, and W are associated was put forward a fairly long time ago, almost immediately after the first attempts to synthesise these compounds in the middle 1950's. However, it was not until more than 15 years had elapsed that the first studies demonstrating the structure of the bismetallocene molecules have been published. The fact that studies in this field using unusually sophisticated experimental techniques began has played a decisive role. Low-valence metallocene complexes of the above elements are extremely sensitive to atmospheric oxygen and moisture and sometimes to molecular nitrogen. In view of the high M–O bond energy, the range of organic solvents which can be used in experiments with these compounds is extremely narrow. It is virtually necessary to confine oneself to saturated and aromatic hydrocarbons and solvents of the ether type. The employment of chromatographic methods of purification with carriers such as alumina, silica gel, and similar substances is not permissible.

The composition of the bismetallocenes obtained at the present time, derivatives of Group IV–VI elements, as a rule corresponds to the formula $(C_{10}H_{10}M)_2$ or differs from it by one, two, or more hydrogen atoms. The data concerning

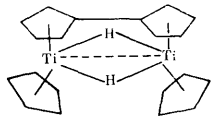
bismetallocenes presented below are arranged in terms of Groups of elements.

## II. BISMETALLOCENE COMPLEXES OF GROUP IV ELEMENTS

### 1. Titanium Compounds

The development of the chemistry of titanocene has been extremely non-uniform and has been distinguished by the publication of a large number of inconsistent results obtained by different investigators. The isolation of the dark-green diamagnetic titanocene $(C_5H_5)_2Ti$ was first reported by Fischer and Wilkinson[14] in 1956. Somewhat later, other investigators[15] who attempted to reproduce this synthesis were unable to isolate the complex of this composition and they therefore raised serious doubts concerning the existence of titanocene. The attempts to synthesise this metallocene were frequently resumed, but the monomeric complex was never obtained. At the present time at least five different bistitanocenes have been described. With serious stipulations, an attempt may be made to regard some of them as identical but the number of undoubtedly different bistitanocenes is even then reduced only to as many as three.

The most thermally stable form of titanocene is the fulvalenetitanium hydride complex $\mu$-($\eta^5$:$\eta^5$-$C_{10}H_8$)-$\mu$-$(H_2)$-($\eta^5$-$C_5H_5)_2Ti_2$:



(V)

The possibility of the formation of this structure was first suggested in 1970.[16] Analysis of the mass spectra[16,17] and infrared spectra[17,18] has played an important role in demonstrating its existence. The infrared spectrum of the complex is characterised by an intense absorption at 1230 $cm^{-1}$ due to the metal–hydride vibration. Important information has also been obtained from an X-ray diffraction study of certain products of the chemical transformation of the stable bistitanocene. However, a study of the $^{13}C$ NMR spectra in 1974 was of decisive importance.[19]

Thus more than 15 years elapsed between the first publication about the synthesis of titanocene and the elucidation of its structure. Approximately the same period was required to determine the necessary experimental conditions for its successful synthesis. In particular, prolonged heating of the reaction mixture or, better, sublimation of the reaction product at temperatures of ~200–220 °C is essential. When this requirement is met, bistitanocene (V) can be synthesised by reducing titanocene dichloride by various reducing agents and also by the thermal decomposition of titanium hydride complexes.

The bistitanocene (V) has been obtained on reducing $Cp_2TiCl_2$ with sodium in toluene with the system heated to 50 °C; the completion of the reaction requires 4 days.[18] Titanocene dichloride is rapidly reduced by sodium in the presence of catalytic[20] or equimolar[21] amounts of naphthalene. Studies have recently been published[17,22] in which $LiAlH_4$ was used as the reducing agent. The stable bistitanocene is formed when the reaction is carried out above 100 °C in cyclo-olefins or aromatic solvents:

$$Cp_2TiCl_2 \xrightarrow{Na,\ or\ Na\text{-}C_{10}H_8,\ or\ LiAlH_4} (V)$$

The stable bistitanocene is also obtained on heating the titanocene hydride $(Cp_2TiH)_2$ [28] above 170 °C or on hydrogenating the dimethyl derivative of titanocene in solution:[24]

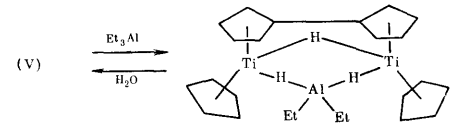
$$(Cp_2TiH)_2 \rightarrow H_2 + Cp_2Ti_2(H)_2\ (\eta^5\text{:}\ \eta^5\text{-}C_{10}H_8);$$

$$Cp_2Ti(Me)_2 + H_2 \rightarrow Cp_2Ti_2(H)_2\ (\eta^5\text{:}\ \eta^5\text{-}C_{10}H_8).$$

The second reaction apparently proceeds via the intermediate formation of the hydride complex $(Cp_2TiH)_2$, which decomposes under the reaction conditions to form the stable bistitanocene; however, the result depends greatly on the reaction conditions (see below).

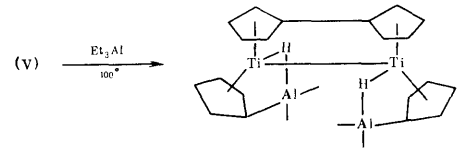
The chemical properties of the bistitanocene (V) have been studied in fair detail. The structures of the products of its reactions with HCl, $H_2O$, and $Et_3Al$ have been established by X-ray diffraction. In all these reactions the dinuclear fulvalene structure is retained.

The interaction of the stable bistitanocene with triethylaluminium under mild conditions (25 °C) yielded the fulvalenetitanium hydride complex,[25] whose hydrolysis under mild conditions regenerates the bistitanocene (V):




(A) $R(Ti\text{–}Ti) = 3.374$ Å

When the reaction was carried out under more severe conditions (100 °C), another fulvalene complex was obtained:[25–27]




(B) $R(Ti\text{–}Ti) = 2.910$ Å

The large difference between the Ti–Ti distances in the structures of compounds (A) and (B) obtained, which are derived from the same initial complex (V), is somewhat unexpected. However, the difference is almost wholly a consequence of the fact that the stereochemical requirements of the Ti–H–Al–$C_{Cp}$ and Ti–H–Al–H–Ti bridging groups are different in the two complexes. The presence of the bridging hydride hydrogen atom in the first structure (A) does not imply the absence of direct Ti–Ti bonding. The three AO in the three-atom system M–H–M (one for each atom) form a single strongly bonding three-centre orbital or two antibonding combinations.[28,29]

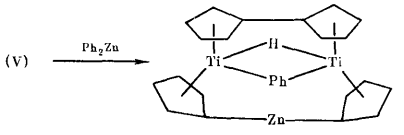
When the system contains only two electrons, only the bonding orbital is filled. In this case the two metal atoms and hydrogen should be located at the corners of a non-equilateral triangle. The addition of a pair of electrons fills one of the antibonding orbitals, i.e. leads formally to the formation of a four-electron three-centre bond. Either the linear configuration (M–H–M) or dissociation of the system with formation of M–H and M is preferable in such a situation. The presence of the direct M–M overlap in the bridging metal hydride complexes has been frequently emphasised in the literature.[28–31]

As already stated, the stable bistitanocene reacts with water[14,21,32] and hydrogen chloride.[14,17,18,21] The products of these reactions, namely $Cp_2Ti_2(\mu\text{-}OH)_2(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)$ [32] and $Cp_2Ti_2(\mu\text{-}Cl)_2(\eta^5\text{:}\eta^5\text{-}C_{10}H_8)$,[33] have the structure of dinuclear fulvalene complexes with bridging hydroxy-groups or with bridging chlorine atoms; the structure has been established by X-ray diffraction. It has been noted that,

on interaction of the stable bistitanocene with HCl, the replacement of bridging hydrogen atoms by bridging chlorine atoms takes place consecutively.[17] The reactions of the fulvalene bistitanocene with HCl and $H_2O$, in which the fulvalene structure is retained and only the bridging hydrogen atoms are replaced by the μ-Cl or μ-OH ligands, are as a whole analogous to the thoroughly investigated reactions of the mononuclear complexes $Cp_2TiX_2$ and $Cp_2TiX$ with nucleophiles.[34]

When the bistitanocene (V) reacts with HCl, the mononuclear complex $Cp_2TiCl_2$ is not formed. This conclusion is important: the metastable titanocene dimers, which are frequently obtained together with the stable isomer, give rise to a high yield of $Cp_2TiCl_2$ in their reactions with HCl, in contrast to the stable isomer. The reaction with hydrogen chloride is therefore a qualitative test for the absence of an admixture of metastable titanocenes in the stable bistitanocene.

Together with the reactions of the stable bistitanocenes examined above, in which the structure of the products has been reliably established, studies have been made where the structure of the products of the reactions of compound (V) cannot be regarded as established. The interaction of the bistitanocene (V) with diphenylzinc yielded the unusual compound [μ-($\eta^5$:$\eta^5$-$C_{10}H_8$)-μ-($\eta^5$-$C_5H_4$Zn-$\eta^5$-$C_5H_4$)(μ-H)(μ-Ph)$Ti_2$], whose structure has been proposed on the basis of the study of the products of its decomposition by heating or by treatment with various chemical reagents.[35] There is no doubt that the proposed structure should be very strained.




When the stable bistitanocene reacts with nitrogen (at a nitrogen pressure of 4 atm) in benzene at room temperature, a nitrogen complex having the composition $C_{20}H_{20}Ti_2(N_2)_2$, whose structure has also not been established, is formed slowly (over a period of three weeks).[36] On reduction with sodionaphthalene and subsequent hydrolysis, the nitrogen complex gives rise to ammonia.[36]

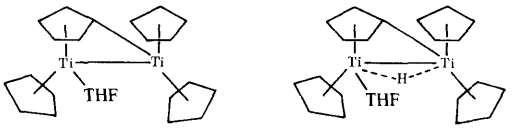
Doubts as to whether the complex is really formed from the molecule of the stable bistitanocene have been raised.[37] One must note that in the first communication concerning the fixation of nitrogen under mild conditions it was already noted that the $Cp_2TiCl_2$–reductant system combined with molecular nitrogen.[38] Later such nitrogen-fixing systems were investigated in many studies (see, for example, Refs. 36–41). In these systems nitrogen is fixed rapidly even at low temperatures and atmospheric nitrogen pressure, while the formation of a complex of the stable bistitanocene and nitrogen is very slow (if it occurs at all).[37] The stable isomer of bistitanocene is chemically fairly inert in the reaction with nitrogen and is apparently not the compound responsible for the effective activation of nitrogen in the $Cp_2TiCl_2$–reductant system.

The stable fulvalene bistitanocene, the synthesis and chemical properties of which were examined above, is the least reactive form of titanocenes. Together with the stable bistitanocene, there exist several highly reactive, so-called "metastable" bistitanocenes. The metastable forms of titanocenes exist at temperatures not exceeding 90 °C; on heating to 100–110 °C, the metastable titanocenes are converted into the stable isomer (V). The properties of the metastable titanocenes are similar but not identical. Nor can one rule out the possibility that in the future, after appropriate checks of the data obtained previously, the number of compounds treated as individual will be reduced.

At least four different metastable isomers of bistitanocene are known: (1) the "low-temperature titanocene" $(C_5H_5)_3$.$(\mu\text{-}C_5H_4)Ti_2$; (2) the "active titanocene" $[(C_5H_5)_2Ti]_{1-2}$; (3) the metastable titanocene" $[(C_5H_5)_2Ti]_2$; (4) the "black titanocene" $(C_{10}H_{10}Ti)_n$ or $(C_{10}H_{9-10}Ti)_n$. Rigorous evidence for the structure is available only for the first of these compounds, obtained in 1976 by the low-temperature reduction of $Cp_2TiCl_2$.[42] Henceforth we shall refer to this form of titanocene as "low-temperature titanocene".

$$Cp_2TiCl_2 + C_{10}H_8\cdot K \xrightarrow{-80^\circ} Cp_3Ti_2\,(\eta^5{:}\ \eta^1\text{-}C_5H_4)\,.$$

The complex obtained is stable in an atmosphere of argon at 20 °C for several days but decomposes in solution, the decomposition being particularly rapid in tetrahydrofuran (THF). The structure of the complex with a THF solvate molecule has been established by X-ray diffraction:[42]




(VIa) $R(Ti\text{-}Ti) = 3.336$ Å (VIb)

In the molecule of compound (VIa) there are two types of titanium atoms—bivalent and tervalent titanium. The $Cp_2Ti^{II}$ species is stabilised by the formation of a Ti–Ti bond and by coordination to the THF molecule. A characteristic feature of this molecule is a high degree of electron unsaturation (a 31-electron complex) and the accessibility of the $Ti^{II}$ atom and the Ti–Ti bond to attack by various reagents. These factors are responsible for the high reactivity of the low-temperature titanocene (VIa) compared with the fulvalene titanocene (V).

The chemical properties of the low-temperature titanocene have been investigated in fair detail. In the majority of reactions the structure of the low-temperature titanocene decomposes with formation of mononuclear biscyclopentadienyltitanium complexes or fulvalene complexes. The THF solvate molecule can be removed by evacuating solutions of the complex in octane. On the basis of infrared spectroscopic data, it is believed that the structure of the complex is then retained. According to Pez,[42] the ease of formation of the non-solvated complex is one of the causes which can explain its high reactivity in relation to compounds such as CO, $N_2$, $H_2$, olefins, etc.

On heating to 110 °C, the low-temperature titanocene is slowly converted into the fulvalene complex (V) in 40% yield:[43]

$$(VI) \xrightarrow[\Delta]{} (V)\,.$$

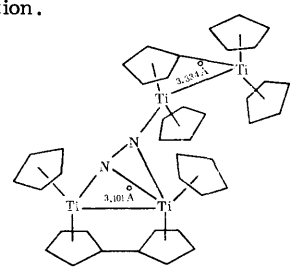
The reactions of compound (VI) with hydrogen chloride, carbon monoxide, ammonia, and hydrogen take place readily and with high yields:[43,44]

$$(VI) \begin{cases} \xrightarrow{HCl} Cp_2TiCl_2 + Cp_2TiCl\,; \\ \xrightarrow{CO} Cp_2Ti(CO)_2\,; \\ \xrightarrow{NH_3} (Cp_2TiNH)_2H\,; \\ \xrightarrow{H_2} (Cp_2TiH)_n\,. \end{cases}$$

In contrast to the stable bistitanocene (V), the low-temperature titanocene (VI) is active in the hydrogenation and isomerisation reactions of unsaturated compounds. Thus compound (VI) catalyses the conversion of ethylene into ethane and buta-1,3-diene.[45]

The high reactivity of the low-temperature titanocene compared with the stable bistitanocene is manifested particularly strikingly in the reaction with molecular nitrogen.

The low-temperature titanocene (VI) reacts with nitrogen even at −80 °C to form a tetranuclear complex with a bridging $N_2$ molecule;[46] its structure has been established by X-ray diffraction.




It is striking that two different bistitanocene fragments are linked by the nitrogen bridge in this molecule: one resembles the low-temperature dimer, while the other is analogous to the molecule of the stable bistitanocene. In discussing the infrared spectrum of this complex and in comparing it with data for other complexes with molecular nitrogen, the authors[46] put forward the interesting idea that the unusually pronounced decrease of the vibration frequency of the N–N bond in some of these complexes, including the compound considered, where $\nu(^{14}N^{14}N) = 1282\ cm^{-1}$ or $\nu(^{15}N^{15}N) = 1240\ cm^{-1}$, is due to the coordination of a nitrogen molecule in these complexes to three metal atoms simultaneously.

It is essential to note a further two significant facts. Firstly, when the N–N bonding [$R$(N–N) = 1.302 Å] is retained in the dinuclear fulvalene fragment of the molecule, the Ti–N and Ti–Ti bonds are unable to be located in a single plane close to the bisector plane of the wedge-shaped sandwiches, as required by the theory and the stereochemical features of the structure of the wedge-shaped sandwiches. Thus the above molecular fragment must be greatly strained. Secondly, the exceptional ease of the transformation of the structure of the low-temperature titanocene with the bridging $\mu$-($\eta^5:\eta^1$-$C_5H_4$) ligand into a structure of the fulvalene type is significantly non-trivial, particularly in view of the fact, mentioned above, that the $Ti(N_2)Ti$ fragment is strained and also the fact that, in the absence of the $N_2$ molecule, the conversion of the low-temperature titanocene (VI) into the fulvalene isomer (V) requires much more severe conditions (temperature ~100 °C) and proceeds at a much lower rate.

The phenomenon of the preferential transformation of the dinuclear metallocene structures with the bridging $\mu$-($\eta^5:\eta^1$-$C_5H_4$) ligands into dinuclear structures with the $\mu$-($\eta^5:\eta^5$-$C_{10}H_8$) bridging fulvalene ligand has been studied in detail in relation to niobocene systems (see below). Regardless of the mechanism of these reactions, the above structural transformations of the dinuclear complexes are always accompanied by the substitution of the metal hydride atoms by other elements capable of playing a much more effective role as bridging ligands; in the first place these are halogen, sulphur, oxygen, nitrogen, etc. atoms. One of the driving forces of these reactions is undoubtedly the energy gain associated with the formation of the M–E–M bridge bonds (where E = halogen, O, S, N, etc.).

In conclusion of the discussion of the available data concerning the structure and properties of the low-temperature titanocene, we shall consider a few more facts. Although for a number of reasons the proposed structure (VIa) is preferable, it is not possible to reject fully the possible presence in the molecule of yet another bridging atom–the hydride hydrogen atom (the location of the hydrogen atoms was not established in the X-ray diffraction study), i.e. the formation of the structure (VIb).

It was established that the interaction of the low-temperature titanocene with HD yields a mixture of gases ($H_2$ + HD + $D_2$), while the reaction with methyl iodide affords methane.[43] In addition there are discrepancies between various spectroscopic properties of the low-temperature titanocene. The hypothesis of the existence of the bridging hydrogen atom agrees with the finding that the infrared spectra of even very pure specimens of the low-temperature dimer always contain an intense absorption at 1230 $cm^{-1}$. The presence of this band cannot be explained (as suggested by Pez[42]) by the presence of an admixture of stable bistitanocene, since according to other estimates its amount cannot exceed several per cent. It may be that the bridging hydrogen atom is present in the molecule of compound (VI) itself. On the other hand, the paramagnetism of the low-temperature bistitanocene agrees well with the structure without a bridging hydrogen atom. However, the conclusion that the complex is paramagnetic is not based on the study of the EPR spectra or a direct measurement of the magnetic moment and was reached only from the change in the positions of the signals of the cyclopentadienyl rings in the $^1H$ NMR spectra as the temperature was altered.[42]

We shall proceed to the consideration of other metastable bistitanocenes. In contrast to compound (VI), obtained by Pez,[42] attempts to establish their exact structure has not been reported.

Van Tamelen et al.[47] investigated the multistage reduction of $Cp_2TiCl_2$ by sodium in toluene, the process being followed by visible and infrared spectroscopy. It was established that different products, which can be isolated, are formed in succession; one of these the authors regard as the "active titanocene":[47] #

$$Cp_2TiCl_2 + 2Na \xrightarrow{20^\circ} [Cp_2Ti]_{1-2}.$$

The results of elemental analysis are not available for this complex, the criteria of its purity and individuality have not been specified, and reactions, sufficiently refined to help in the elucidation of its structure, have not been found. Nevertheless, it has been demonstrated that the complex $[Cp_2Ti]_{1-2}$ is metastable and is converted into the stable bistitanocene on prolonged stirring in solutions with sodium or on heating to 100 °C. Its properties have been described extremely briefly.[47] Thus it has been reported that the reaction with HCl leads to $Cp_2TiCl_2$, while the reaction with CO yields $Cp_2Ti(CO)_2$. The complex catalyses the hydrogenation of olefins at atmospheric hydrogen pressure and is capable of forming a complex with nitrogen having the tentative composition $Cp_2Ti{-}N{=}N{-}TiCp_2$.

A highly reactive titanocene complex, called "metastable titanocene", was obtained in 1971 as a result of the slow spontaneous decomposition of a suspension of the grey-green polymeric hydride $(Cp_2TiH)_x$ § in toluene.[11,23] The process proceeds with evolution of hydrogen:

$$Cp_2Ti(Me)_2 \xrightarrow[0^\circ]{H_2} (Cp_2TiH)_n \rightarrow (C_5H_5Ti)_2 + H_2.$$

The complex has an intense dark colour with a greenish tint; measurement of its molecular weight showed that it is dimeric and has the tentative composition $C_{20}H_{20}Ti_2$. Measurement

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#The reduction of $Cp_2TiCl_2$ by sodium amalgam and the Na/K alloy has been mentioned;[48–51] the structures of the products of these reactions have not been established.

§The polymeric hydride $(Cp_2TiH)_x$ is characterised by an intense Ti–H absorption at 1140 $cm^{-1}$, in contrast to the dimeric hydride $(Cp_2TiH)_2$, in the spectrum of which the Ti–H absorption band is at 1450 $cm^{-1}$.[12,23]

of its magnetic susceptibility demonstrated that it is paramagnetic. The complex could not be isolated from solution in the crystalline state and its elemental composition was not therefore analysed; it is not known whether one or several compounds are present in solution. We may note that conclusive evidence concerning the structure and individuality of the polymeric hydride $(Cp_2TiH)_n$ is not available either.

The chemical properties of this bistitanocene have been investigated in fair detail; all the reactions quoted below take place readily and with high yields:[11,23,52]

$$\begin{array}{l} (Cp_2Ti)_2O \xleftarrow{N_2O} \\ (Cp_2TiH)_n \xleftrightarrow{H_2} \\ Cp_2Ti(CO)_2 \xleftarrow{CO} \end{array} \Bigg| \longrightarrow [(C_5H_5)_2Ti]_2 \longrightarrow \begin{array}{l} \xrightleftharpoons{N_2} (Cp_2Ti)_2N_2; \\ \xrightarrow{HCl} Cp_2TiCl_2; \\ \xrightarrow{PPh_3} C_{10}H_{10}TiPPh_3. \end{array}$$

It is striking that the reactions of all the metastable titanocenes described above with HCl and CO proceed in the same way. The so-called "black titanocene", obtained by the photolysis of dimethyltitanocene,[53] i.e.

$$Cp_2Ti(Me)_2 \xrightarrow[\text{solvent}]{h\nu} (C_{10}H_{10}Ti)_n + CH_4^{\cdot},$$

also reacts analogously with the above reagents.

The authors themselves[53] initially suggested that the "black titanocene" which they obtained is analogous to the metastable titanocene synthesised previously.[11,23] However, in contrast to the latter the "black titanocene" is diamagnetic and the $^1H$ NMR spectra of its solutions contain signals due to the Cp protons (albeit broadened). The structure of the complex has not been discussed in detail and there is also uncertainty as regards its composition: $[C_{10}H_{10}Ti]_2$ or $[C_{10}H_{9-10}Ti]_2$. The complex is much less volatile than the stable bistitanocene. It was found unexpectedly that its interaction with molecular nitrogen leads to the formation of a dark-red compound. In a later investigation[54] the same workers reported the isolation of a very similar but not identical compound on photochemical decomposition of $Cp_2TiPh_2$.[54] However, it was suggested almost simultaneously[55] that the "black titanocene" is in essence the polymeric compound $[Cp_2TiH]_n$.

All four metastable titanocenes described above are reactive towards molecular nitrogen. Complexes of different compositions have been described and it has been established that treatment of these complexes with reducing agents and subsequent hydrolysis lead to the evolution of ammonia or hydrazine. These investigations have been analysed in detail in a communication[37] whose authors have been actively engaged in this field recently.¶ Only those data are important to us which make it possible to compare the metastable titanocenes with one another. In particular the "metastable titanocene"[11,23] has properties resembling those of the "low-temperature titanocene".[42] Their reactions with $H_2$, $N_2$, HCl, and CO are also similar; their infrared spectra and the spectra of the products of their reactions with $H_2$ and $N_2$ are likewise similar but not identical. Both compounds form adducts with THF.[12,42,43] One can also assume that the "active titanocene" is identical with the "low-temperature titanocene".[47] The infrared and ultraviolet spectroscopic characteristics of both the initial complex and of its compounds with nitrogen are similar. On the other hand, in terms of a series of other characteristics discussed above, these compounds are not identical or cannot be compared. The greatest uncertainty concerns the "black titanocene".[53] All its reported characteristics differ from those of the other isomers of bistitanocene.

In conclusion, it is appropriate to mention yet again that the metastable bistitanocenes are highly reactive compounds and that in many cases this might have led to methodological errors in the formulation of the experiments and hence to an incorrect interpretation of some of the results.

Titanocenes whose nature is close to that of the metastable complexes discussed above have also been obtained in studies of the thermal decomposition of titanocene derivatives of the type $Cp_2TiR_2$, where R is an organic or organoelemental group. Depending on the substituents, the decomposition of the complexes $Cp_2TiR_2$ is carried out at room temperature (R = $CH_2Ph$,[56] $SnEt_3$, $GeEt_3$, or $SiEt_3$ [57]) or on heating to 70–90 °C (R = Me or Ph [58,59]). It was assumed that initially the thermolysis proceeds in the same way in all cases:

$$Cp_2TiR_2 \rightarrow (C_{10}H_{10}Ti)_n + R^{\cdot},$$

The reactions result in the formation of highly reactive titanocenes sometimes containing THF solvate molecules. The possible structures of the complexes have not been discussed and the formulae of the compounds ($Cp_2Ti$ and $Cp_2Ti$. .THF) were proposed mainly on the basis of the microanalytical determination of their metal content.

The following reactions have been achieved for the titanocenes obtained in this way:[58–62]

$$(C_{10}H_{10}Ti)_n \Bigg| \begin{array}{ll} \xrightarrow{PhCH_2Cl} & Cp_2TiCl_2; \ \text{(Ref.58)} \\ \xrightarrow{HCl} & Cp_2TiCl_2; \ \text{(Ref.59)} \\ \xrightarrow{RCCl_3} & Cp_2TiCl_2; \ \text{(Ref.59)} \\ \xrightarrow{(PhCOO)_2} & Cp_2Ti(OCOPh)_2; \ \text{(Ref.60)} \\ \xrightarrow{H_2C_2Cl_2} & Cp_2TiCl_2; \ \text{(Ref.61)} \\ \xrightarrow{Ph_3CCl} & Cp_2TiCl_2 + CpTi(Cl)CPh_3. \ \text{(Ref.62)} \end{array}$$

All these reactions with reagents tending to interact via the oxidative addition mechanism proceed readily; they all result in the formation of isotypical mononuclear titanocene derivatives and the yields of the products are frequently high.

Later investigations of the thermal decomposition reactions of the titanocene derivatives $Cp_2TiR_2$ showed, however, that the abstraction of the groups R from the $Cp_2TiR_2$ molecules is followed by a hydride shift from the cyclopentadienyl ring to the titanium atom;[63] thus, the structure of the reaction products is undoubtedly more complex than $Cp_2Ti$ or $Cp_2Ti$. .THF, although it has not yet been established.

The reactions of titanocenes obtained by reducing $Cp_2TiCl_2$ with boron disulphides, diselenides,[64] and halides[65] have also been achieved:

$$(C_{10}H_{10}Ti)_n \Bigg| \begin{array}{ll} \xrightarrow{RS-SR} & Cp_2Ti(SR)_2, \\ \xrightarrow{YBX_2} & Cp_2Ti(Y)BX_2. \end{array}$$

Unfortunately the relevant communications contain no information which would make it possible to determine the type and quality of the titanocenes with which the authors worked; one cannot rule out the possibility that they dealt with a mixture of isomers.

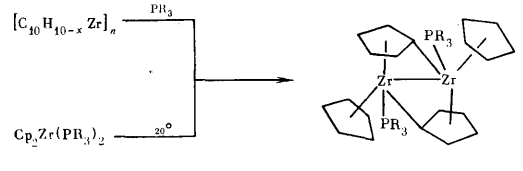
¶ We may point out that the majority of the nitrogen-containing complexes of titanocene and their derivatives, whose structure has been established fairly reliably in one way or another, are dinuclear compounds. However, the dinuclear nature of the structures arises precisely and solely as a result of the 1,2-bidentate nature of the $N_2$ ligand, which entails the formation of the long Ti–N–N–Ti bridge. Examination of this mode of formation of the dinuclear structures is outside the framework of this review, but the synthesis is nevertheless almost always based on mononuclear titanium compounds. Such structures differ little from other bridged structures with long bidentate or polydentate ligands of the type M–L–L–M.

## 2. Compounds of Zirconium and Hafnium

Zirconium and hafnium bismetallocenes have been investigated to a much lesser extent than the corresponding titanium derivatives. The increase of the atomic radius on passing from titanium (1.45 Å) to zirconium and hafnium (~1.60 Å), while the structures of the outer electronic levels are the same ($d^2s^2$ or $d^4$), leads to an increase of coordinating capacity on passing from Ti to Zr and Hf; the ionisation potentials of the atoms diminish in the same sequence. Accordingly, compounds of the type $Cp_2MX_2$ are more stable for the heavy elements. It has also been noted that the dialkyl and diaryl derivatives of zirconocene and hafnocene $Cp_2MR_2$, where R = alkyl or aryl, are thermally more stable than the corresponding titanium compounds.[66]

The methods used to synthesise the zirconium and hafnium metallocenes are on the whole analogous to those employed for the synthesis of bistitanocenes. The reduction reactions of the dihalides $Cp_2MCl_2$,[20,25,67,68] the thermal decomposition reactions of the dialkyl compounds $Cp_2M(Alk)_2$ and the alkyl hydride complexes,[53,69,70] as well as the reduction reactions involving the cleavage of the dimethylmetallocenes $Cp_2M(Me)_2$ by triethyltin and triethylgermanium hydrides[71] have been investigated. All the reactions led to similar but not identical compounds. The attempts to obtain crystals suitable for X-ray diffraction studies were unsuccessful. The hypothesis that the zirconocene and hafnocene structures are identical with the structure of the stable bistitanocene has not received serious confirmation.

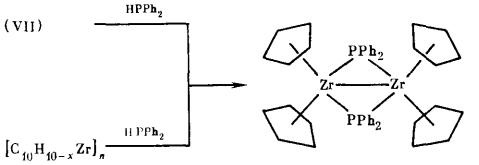
The majority of the investigations have been carried out with zirconium derivatives. However, the data available at present are insufficient to attribute a specific structure to these compounds with adequate confidence. There are also no reliable grounds for the assumption that these compounds are chemically individual (although it is quite natural that, in the analysis of their reactions, the discussion is conducted from the standpoint of their individuality). The presence of an intense absorption band in the infrared spectra of the zirconocenes isolated in the range 1250–1300 $cm^{-1}$, which disappears after only brief contact of the compounds with air, has been noted. The band occurs in the region characteristic of the Zr–H–Zr bridging fragments.[70,72] Its great width is most probably due to the indeterminate oligomeric character of the structures, which leads to the non-equivalence of the crystal-chemical environments of the hydride atoms. In solution, the zirconium compounds are unstable and give rise slowly to insoluble polymers. It has been found[70,73,74] that the zirconocenes obtained by different methods react with phosphines ($PMe_2Ph$ and $PPh_2Me$) at 50–60 °C to form the dinuclear zirconocene complexes $[Cp_2.(\mu\text{-}C_5H_4)_2Zr(PR_3)_2]$ in 30–50% yields; the processes are accompanied by the evolution of hydrogen. This readily occurring reaction constitutes in fact the main objection to the hypothesis that the zirconocene has a structure analogous to that of the stable bistitanocene (V).




(VII)

The thermal decomposition of the mononuclear zirconocene-phosphine complexes $Cp_2Zr(PR_3)_2$ leads to the same biszirconocene–bisphosphine product in a high yield.[73,74] The structure of the complex (VII) has been postulated on the basis of the study of its NMR spectra. It is shown below that this complex can be regarded as a kind of structural and electronic analogue of the bisniobocene (XIV).

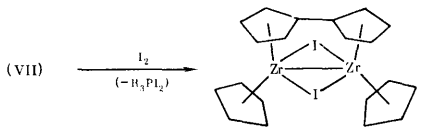
Treatment of compound (VII) with diphenylphosphine ($Ph_2PH$), which contains a mobile hydrogen atom, results in a very ready cleavage of the Zr–C σ-bonds and the formation of the dinuclear phosphide complex (VIII), whose cyclopentadienyl ligands contain only hydrogen atoms as substituents.[74] However, this reaction is not unambiguous, since the complex $[(C_5H_4)_2Cp_2Zr_2(PHPh_2)_2]_n$ is formed in addition to compound (VIII).




(VIII)

The complex (VIII)† is also formed when oligomeric zirconocenes are treated with $Ph_2PH$.

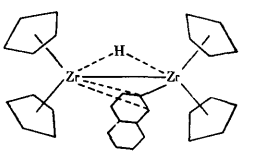
The only example of a dinuclear fulvalene derivative of zirconocene is compound (IX) obtained by treating compound (VII) with iodine at a temperature below −50 °C. The complex (VIII) is diamagnetic, is weakly associated in solution, and, according to $^1H$ and $^{13}C$ NMR spectra, has a structure analogous to the fulvalene bistitanocene (V):[74]




(IX)

It must be assumed that, as in compound (V), a direct metal–metal bond should be present in the complex (IX).

In conclusion of this Section, we may mention a recently published study[76] in which an attempt was made to synthesize monomeric zirconocene by the low-temperature reduction of $Cp_2ZrCl_2$ with potassionaphthalene in THF at −80 °C. The reaction led to the unexpected dinuclear complex (X) with a bridging β-naphthyl group and hydride hydrogen:




(X) $R(Zr\text{-}Zr) = 3.307$ Å

The presence of hydride hydrogen was demonstrated by $^1H$ NMR and by chemical methods. At room temperature the complex (X) decomposes slowly, giving rise to unknown products. Treatment of the complex with HCl produces $Cp_2ZrCl_2$ and a mixture of hydrogenated naphthalenes ($C_{10}H_{10}$, $C_{10}H_{12}$, and $C_{10}H_8$). Comparison of the properties of compound (X) and the "low-temperature" bistitanocene as hydrogenation catalysts showed that the effectiveness of compound (X) in this reaction is incomparably lower.[76]

As regards the chemistry of the bismetallocene complexes of Group IV elements, one should also note than an increasing number of studies of the reactions of compounds contain-

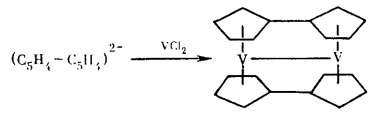
†Such complexes had been obtained earlier from $Cp_2ZrCl_2$ and $LiPR_2$.[75]

ing the $\eta$-$C_5Me_5$ ligands instead of the $\eta$-$C_5H_5$ ligands have been published in recent years. It has been established that the hydrogen atoms of the methyl groups are directly involved in many reactions of these metallocene derivatives, but the compounds formed are as a rule mononuclear and their structures have nothing in common with those discussed above. For this reason, we have in fact not considered these data; most of such studies have been surveyed in another review.[37]

## III. BISMETALLOCENE COMPLEXES OF GROUP V ELEMENTS

Numerous dinuclear metallocene derivatives can be obtained comparatively readily for heavy Group V elements—niobium and tantalum. On the other hand, the formation of bismetallocene complexes, resulting from the combination of mononuclear molecules, has not so far been observed for vanadium. Simple vanadium compounds such as $Cp_2V$,[1,77] $Cp_2VR$,[1,78,79] $Cp_2VX$,[1,80] and $Cp_2VR_2$[1,81] are monomeric both in solution and in the crystalline state and are not converted into dinuclear structures even under severe conditions. One of the most important causes of this is the marked coordination shielding of the small vanadium atom. All reactions whose mechanisms involve a stage in which there is a significant expansion of the coordination sphere of the metal are apparently extremely energetically unfavourable. Reactions which do not incorporate such a stage proceed readily and lead to complexes with coordination numbers typical for vanadium.

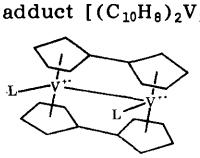
There has been only one study devoted to the synthesis of bismetallocene derivatives of vanadium.[82,83] The key compound in this investigation was difulvalenedivanadium, which has been synthesised in a high yield from the vanadium salt $VCl_2$ and the fulvalene dianion $(C_5H_4-C_5H_4)^{2-}$:



(XI)

As for the monovanadocene complexes, the coordinating capacity of the metal atom in this compound has been to a significant extent exhausted. Accordingly, the chemical properties of the complex (XI) have nothing in common with those observed for compounds of the Ti, Zr, and Hf series.

Difulvalenedivanadium (XI) and its dicarbonyl derivative $(C_{10}H_8)_2V_2(CO)_2$ are diamagnetic,[83] and in contrast to the related complexes of monomeric vanadocene. The mono- and di-cationic compounds $[(C_{10}H_8)_2V_2]^{n+}$, where $n = 1$ or 2, and $[(C_{10}H_8)_2V_2L_2]^{n+}$, where $n = 1$ or 2 and L = CO or $NCCH_3$, obtained from them are also either diamagnetic or their magnetic susceptibility is low, which distinguishes them sharply from the related derivatives of mononuclear vanadocene. The dicationic adduct $[(C_{10}H_8)_2V_2(NCCH_3)_2]^{2+}(PF_6^-)_2$,[82] i.e.



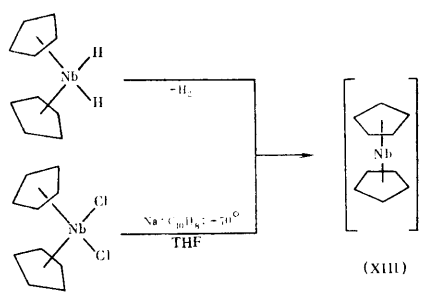
(XII) $R(V-V)=3.329$ Å

has been studied by X-ray diffraction. Crystallographic data for compound (XII) as well as analysis[83] of the electronic absorption spectra and the magnetic behaviour of other dinuclear complexes are consistent with the occurrence of a direct bonding interaction between the vanadium atoms.

Analogous difulvalene compounds of the elements in the second and third transition series are unknown for both Group V and Group IV elements examined above.

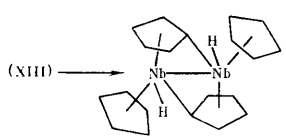
A different picture has been observed for niobium derivatives (there are very few data on the tantalum compounds[84]). There are numerous elements of similarity in the structure and characteristic features of the reactions of the bismetallocene compounds of Ti, Zr, Hf, Nb, and Ta (and, as will be shown below, also Mo and W). However, the first characteristic which draws attention is the fact that the dinuclear compounds are readily formed when attempts are made to synthesise the mononuclear metallocenes. The observed structural and chemical differences between the isoligand dinuclear complexes of different metals are fairly simply and unambiguously related to the electronic configuration of the atoms of these metals, which have different numbers of intrinsic valence electrons depending on the Group.

Like the Group IV elements, niobium and tantalum do not form homoligand mononuclear metallocenes of the type $Cp_2M$ which are stable at room temperature. However, at low temperatures a niobium complex having this particular composition can in fact be detected in solution by EPR.[85-87] It may be that this fact manifests objectively the lower reactivity of the mononuclear metallocenes of the Group V metals caused by their lower electron deficiency.



(XIII)

The monomeric niobocene (XIII) is comparatively stable at temperatures below −60 °C; an increase of temperature entails its rapid and easy conversion into the bisniobocene (XIV):[85,86]



(XIV) $R(Nb-Nb)=3.105$ Å

This reaction is of second order with respect to the monomeric complex and is so far the only known example confirming directly the possibility of the formation of bismetallocenes considered via the dimerisation of the monomeric homoligand metallocenes $(\eta\text{-Cp})_2M$.[86] In essence this is an oxidative addition reaction involving the C–H bonds of another niobocene fragment.# Furthermore the Nb–Nb bond is formed in compound (XIV) despite the fact that the resulting structure is sterically very strained. Overall, the effective atomic number rule holds for the niobium atoms in compound (XIV) and these atoms thus make use of their coordinating and valence capacities in bonding.

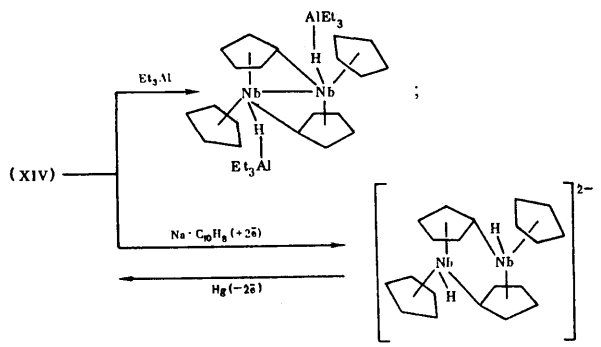
#We may note that other oxidative addition reactions are also known for compound (XII), which, however, have no bearing on the subject of this review.[3]

We may note that the bisniobocene (XIV) was the first compound among the dinuclear metallocene complexes of Group IV–VI elements whose structure and dinuclear nature have been established by direct investigation.[88,89] It was in fact after these publications that all the early studies where the formation of coordination- and electron-deficient mononuclear complexes had been unjustifiably postulated for Group IV–VI elements were re-examined and retested.

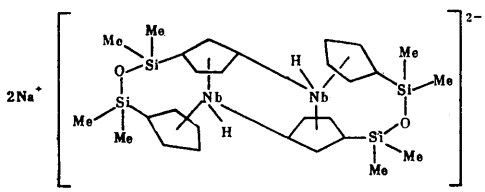
The structure of the bisniobocene (XIV) has different elements of similarity with the "low-temperature" bistitanocene (VI). However, in contrast to the latter, the bisniobocene (XIV) is thermally entirely stable and does not isomerise to a complex with the fulvalene ligand analogous to compound (V) even after prolonged heating to 200–250 °C. The explanation of this difference in the behaviour of compounds (VI) and (XIV) is that the direct thermal rearrangement to the fulvalene dimer $[(Cp)_2(C_5H_4{-}C_5H_4)Nb_2(H)_2]$ is unfavourable for the bisniobocene (XIV) as a consequence of the overall loss of bonding energy. However, we showed in our later studies (see the appendix at the end of the review) that the indirect two-stage conversion of compound (XIV) into a fulvalene complex of this kind takes place readily; it entails the intermediate synthesis of a dinuclear halogeno-derivative.

The majority of the reactions of the bisniobocene (XIV), like those of the titanium subgroup derivatives, are many-centre processes and involve the entire system of σ-bonds (i.e. the M–M, M–C, and M–H σ-bonds) in the central fragment of this compound. On the whole, this is not surprising, since such molecular fragments are none other than heteronuclear clusters in which the simultaneous rearrangement of a large number of chemical bonds constitutes a common phenomenon. The local transformations involving one atom or one bond are not then ruled out, but the range of reagents capable of effecting such reactions is sharply reduced.

It has been noted for only two reactions of the bisniobocene (XIV) that the nature of the ligand groups does not change. Thus the interaction of compound (XIV) with $Et_3Al$ involves only the Nb–H hydride atoms and converts them into the Nb–H–Al bridge group.[90] On the other hand, treatment of compound (XIV) with strong electron donors leads to the formation of dianionic complexes.[91] In the latter case the reverse reaction also takes place quantitatively.



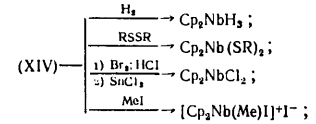

The disodium salt of silylbisniobocene has been investigated by X-ray diffraction.[91]




(XV) $R(Nb{-}Nb) = 3.932$ Å

Compared with the neutral bisniobocene, the corresponding dianionic complexes (XV) are characterised by significantly greater interatomic distances M...M, which can no longer be regarded as metal–metal bonds. As a consequence, there is virtually no steric strain in the structure of the dianions. The additional electrons are thus transferred to the antibonding $\sigma^*_{MM}$ molecular orbital. This conclusion has been confirmed unambiguously by a study of the electronic spectra of the neutral and anionic complexes.[91]

One of the most characteristic many-centre reactions of the bisniobocene (XIV) is its ready decomposition to the mononuclear derivatives $Cp_2NbX_2$. These reactions are rapid and smooth and the yields of the final products are extremely high.[3,84]

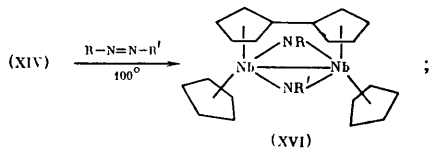



$Cp_2NbH_3$; $Cp_2Nb(SR)_2$; $Cp_2NbCl_2$; $[Cp_2Nb(Me)I]^+I^-$;

R = aryl or ferrocenyl.

It should be specially noted that the products of these reactions contain no substituents in the cyclopentadienyl rings other than hydrogen. We have already encountered a similar fact in relation to the individual reactions of the complexes (VI) and (VII), but, in view of the small number of available observations and the low yields of the final products, great importance could not be attributed to such reactions. The results obtained for bisniobocene show that these reactions occur consistently, but their mechanism is at present unknown. The main feature which must be established is whether individual stages of these processes can be discovered and then carried out as independent reactions (see the appendix below).

Another type of many-centre reactions of bisniobocene comprises those which lead to dinuclear complexes with the fulvalene ligand. As noted above in the discussion of the complexes of titanocenes with molecular nitrogen, such rearrangements are very strongly promoted by the presence in the coordination sphere of the metal of atoms capable of acting as effective bridging ligands; these are usually halogen, oxygen, sulphur, and nitrogen atoms. This approach has been specifically and widely used in the synthesis of fulvalene derivatives of niobium. Thus the interaction of compound (XIV) with aromatic azo-compounds led to fulvalene complexes with two bridging nitrene ligands:[92]




(XVI)

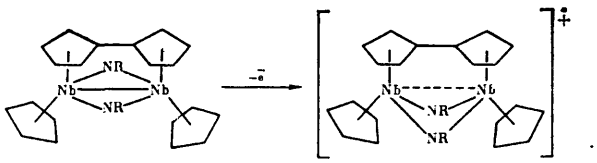
(a) $R = R' = Ph, C_6H_4Me, C_6H_4OMe$;

(b) $R = Ph$, $R' = C_6H_4NMe_2$.

The use of an asymmetric azo-derivative made it possible to obtain a compound with two different nitrene ligands.

The complexes (XVI) proved to be very interesting subjects for spectroscopic, structural, and chemical studies.[93,94] The presence of the direct metal–metal bond and the stereochemical and electronic saturation of the coordination spheres of the metal atoms determine all the characteristic features of their structure and behaviour. Among all the dinuclear metallocene complexes examined in the present review, these are the only compounds which are entirely stable in air even at elevated temperatures (250 °C). They withstand chromatographic purification on $Al_2O_3$ and readily sublime *in vacuo*.

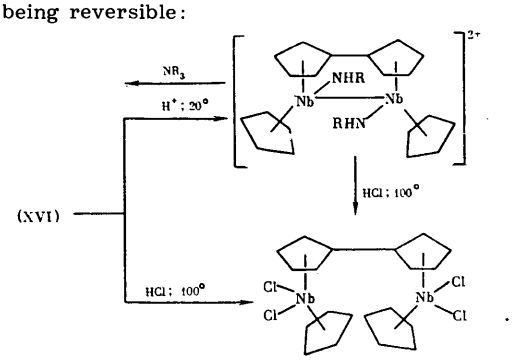
The one-electron oxidation of the fulvalenenitreneniobium complexes (XVI) by ferrocenium salts, mercury and silver salts, and atmospheric oxygen in an acid medium takes place quantitatively.[94] This has led to the synthesis of a whole series of salts of the complex radical-cations (XVII) which are stable in air.



(XVIa) $R(Nb-Nb)=2.834$ Å (XVII) $R(Nb-Nb)=2.921$ Å

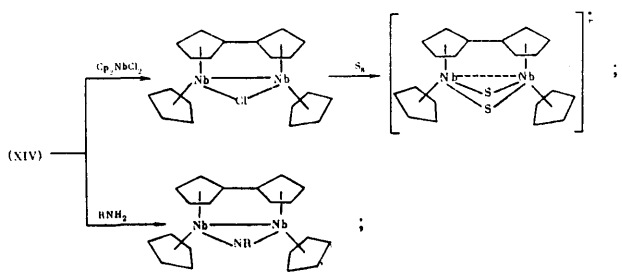
Comparison of the structures and the electronic spectra of the complexes (XVI) and (XVII) established that the electron is eliminated from the metal–metal bond.[94]

Protonation of compound (XVI) by dilute solutions of strong acids under mild conditions converts them into dicationic complexes with terminal nitrogen-containing ligands, the process being reversible:



Under severe conditions (~100 °C) in the presence of an excess of acid and anions which are powerful nucleophiles the nitrene ligands are split off irreversibly.[93]

Another series of dinuclear fulvalene complexes have been obtained from the bisniobocene (XIV), namely compounds with a single bridging heteroligand. Two types of such compounds have been obtained: diamagnetic with a single bridging nitrene two-electron-donating ligand[95] and paramagnetic with a bridging halogen atom—a three-electron-donating ligand:[96,97]



R = Ph, $C_6H_4Me$, $C_6H_4N_2Ph$.

The chlorine-containing single-bridge complex is converted by elemental sulphur into a disulphide radical-cation complex, which is an analogue of the radical-cation dinitrene compound (XVII).[98]

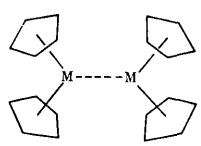
Comparison of the overall data on the bismetallocenes of Group IV and V elements shows that throughout the period of the development of the research into the Group IV elements, most effort has been directed to the determination of the structures of the key compounds. In the case of the Group V compounds the situation is different; the structure of the compounds was established comparatively rapidly and investigations were concentrated mainly on the characteristic features of their chemical reactions.

## IV. BISMETALLOCENE COMPLEXES OF GROUP VI ELEMENTS

The first bismetallocene compounds of Group VI metals were synthesised approximately 10 years ago and the most intense research has been prosecuted during the last five years. As for the Group V compounds, among the derivatives of the Group VI elements dinuclear complexes with a wide variety of structures are formed readily only by the heavy elements—molybdenum and tungsten. On the other hand, as in the case of vanadium,[1] the formation of bismetallocene compounds is altogether uncharacteristic of chromium.[2] The only exception is difulvalenedichromium,[99] which is discussed below after the monofulvalene derivatives; data on the difulvalenedimolybdenum compounds are also presented.[100]

The monomeric homoligand molybdenocene and tungstocene were obtained in 1979 by the low-temperature photolysis of $Cp_2MH_2$ and $Cp_2M(CO)$ and have been detected spectroscopically (on the basis of infrared spectroscopic data) in an argon matrix at 10 K.[4] The claims concerning the formation of derivatives having the composition $C_{10}H_{10}M$ prior to the above study refer, as is now clear, to compounds having a more complex structure; the monomeric compounds $C_{10}H_{10}M$ are indeed formed but only as extremely labile intermediates which cannot be detected by physical methods. It has been found that, on raising the temperature, the monomeric molybdenocene and tungstocene undergo irreversible association to form complexes $(Cp_2M)_x$ of unknown structure—tentatively dimers.[101,102] It may be that these compounds are identical with complexes having the same composition and obtained previously by the reduction of $Cp_2MCl_2$ with sodium amalgam.[103,104] In the mass spectra of the complexes $(Cp_2M)_x$, obtained by reducing metallocene dihalides, the $C_{20}H_{20}M_2^+$ ion is heaviest, while the $^1H$ NMR spectra of solutions of these compounds exhibit only one signal due to the protons of the unsubstituted cyclopentadienyl rings.[104]

For a long time, the above derivatives were the only bismetallocene complexes whose association was tentatively assumed to occur only as a result of metal–metal bonding. Analogous evidence has now been obtained also for rheniocene (see the appendix below).



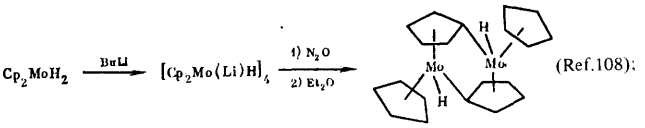
(XVIII)

The chemical behaviour of the complexes (XVIII) is characterised by an extremely ready conversion into mononuclear derivatives on interaction with a wide variety of compounds in which they behave as carbene-like species.[103–107] The reaction products are complexes of the type $Cp_2M(L)_n$ ($n$ = 1 when L is a two-electron-donating ligand and $n$ = 2 when L is a one-electron-donating group).

Attention has been drawn to the fact[105,107] that the rearrangement of these associated species to other bismetallocenes, whose structures include bridging $\eta^5:\eta^1$-$C_5H_4$ and $\eta^5:\eta^5$-$C_5H_4$-$C_5H_4$ ligands, does not take place. This is surprising because many compounds with such bridging groups are known for both molybdenum and tungsten and the latter complexes readily undergo interconversions.

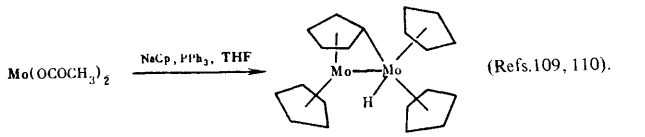
The bismetallocenes of molybdenum and tungsten with the $\eta^5:\eta^1$-$C_5H_4$ and $\eta^5:\eta^5$-$C_5H_4$–$C_5H_4$ ligands have now been investigated in fair detail. Their structure and interconversions follow the same rules, as regards their most fundamental aspects, which were manifested in the behaviour of the isoligand complexes of Group IV and V metals.

Two reactions, which make it possible to obtain dinuclear compounds with bridging $\eta^5:\eta^1$-$C_5H_4$ ligands, are known for molybdenocene derivatives:




(Ref.108);

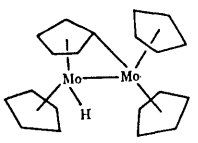
(XIX)




(Refs.109, 110).

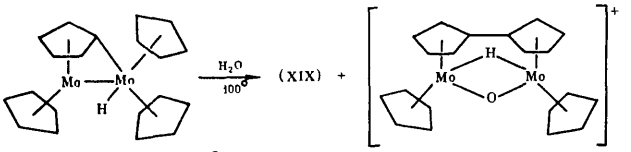
(XXa)

The bismolybdenum complex (XIX) resembles the bisniobocene (XIV), while the other compound (XXa) is similar to the "low-temperature" isomer of the bistitanocene (V). Compound (XXa) has also been converted into the complex (XIX) by heating a suspension of compound (XX) in water at 100 °C.[110]



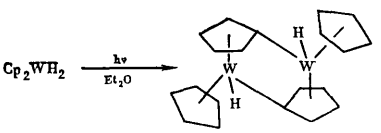

(XXb)

As shown below, the process leads to a mixture of two products. Compound (XXa) is apparently converted into compound (XIX) directly in the crystal phase, while the second compound is formed on interaction of compound (XX) with water. The structures of the complexes were determined from infrared spectroscopic, NMR, and mass spectrometric data and for compound (XXa) an X-ray diffraction study was carried out in addition.[109,110] However, the locations of the hydrogen atoms could not be determined in the course of the structural study. The association of the hydride hydrogen with the molybdenum atom can therefore be regarded merely as being most probable on the basis of a set of spectroscopic and stereochemical considerations but has been by no means finally demonstrated. The structure (XXb) is possible as an alternative.




(XXa) $R$(Mo–Mo)=3.189 Å

The bistungstocene (XXI) has been obtained by the photolysis of tungstocene dihydride in ether and also by its thermolysis in cyclohexane.[111,112] The structure of the product has been demonstrated by X-ray diffraction:[101]



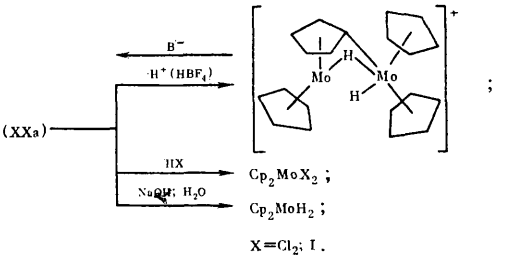

(XXI) $R$(W–W)=3.81 Å

Its photolysis or thermolysis in the presence of tetramethylsilane led to the synthesis of the related *cis*- and *trans*-isomeric products $(C_5H_5)(Me_3SiCH_2)W(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4)_2W(H).(C_5H_5)$.[101,111] The methyl analogue $(C_5H_5)MeW(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4)_2W(C_2H_5)(H)$ has also been obtained by the thermolysis of $Cp_2WH(Me)$.[112]

In discussing the mechanisms of these reactions, it has been suggested[111,112] that they all include a stage involving the formation of the free metallocenes $(\eta^5\text{-}C_5H_5)_2M$, because otherwise the complexes (XIX), (XX), and (XXI) should have been readily obtained from the monomeric molybdenocene and tungstocene, whose existence has been demonstrated. It has been postulated[101,108–112] that the dimers (XIX)–(XXI) listed above arise not from the free mononuclear metallocenes but from their highly reactive adducts (having a wedge-shaped structure) with molecular nitrogen [in the synthesis of compound (XIX)], with triphenylphosphine [in the formation of compound (XXI)], or, finally, with solvent molecules [in the formation of compound (XXI)]. However, there is no reliable experimental confirmation of these hypotheses.

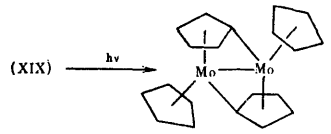
Further chemical reactions of the dinuclear compounds with bridging $\eta^5$-$C_5H_4$ ligands resemble the familiar reactions of the corresponding bistitanocene and bisniobocene complexes. The differences observed in these reactions are due to the increase of the number of intrinsic electrons in each metal atom in the series of derivatives of Group IV, V, and VI elements or, in other words, to the decrease of the electron deficiency of the metallic centre. In the molybdenum and tungsten compounds this is responsible for the resulting decrease of the maximum number of possible chemical bonds. Such a decrease entails a smaller steric strain in virtually all the dinuclear derivatives of molybdenum and tungsten compared with the analogous isoligand complexes of Group IV and V metals. A second characteristic feature, an overall appreciable decrease of the reactivity of the bismetallocene compounds on passing to derivatives of Group VI elements and also a significant decrease of the proportion of many-centre reactions of such compounds, is directly related to the first feature described above. Thus molybdenum and tungsten complexes are as a rule fairly resistant to reaction with water and acids (even at elevated temperatures), while the decomposition of the titanium, zirconium, hafnium, niobium, and tantalum compounds proceeds very readily and is frequently accompanied by the loss of cyclopentadienyl ligands. Reactions involving individual bonds, in the first place M–M and M–H bonds, can be achieved much more readily having molybdenum and tungsten complexes.

The complex (XXa) is readily and reversibly protonated. On the other hand, when acids whose anions are powerful nucleophiles are used for the protonation, the dinuclear structure is completely cleaved:[109,110]




Treatment of compound (XXa) with aqueous alkali unexpectedly led to the formation of the mononuclear molybdenocene dihydride.[110] In relation to the metal atoms, this is in essence a disproportionation reaction, although the nature of the metal-containing products has not been established.

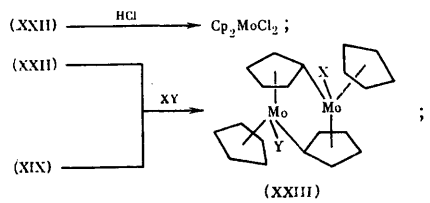
The structures of the complexes (XIX) and (XXI) are analogous to that of the dianionic bisniobocene derivative (XV). This is not surprising, since all these compounds contain identical ligand groups and are isoelectronic. On the other hand, the oxidised dicationic derivatives of the bismolybdenocene (XIX) and the bistungstocene (XXI) should apparently be isoelectronic and apparently isostructural with the neutral bisniobocenes (XIV). However, the oxidation reactions of molybdenocene and tungstocene have not been investigated. At the same time, the photochemical dehydrogenation of compound (XIX) has been achieved.[102,110,113]




(XXII) $R(Mo-Mo)=2.886$ Å

The structure of compound (XXII) isolated in this reaction, which the authors called "dehydromolybdenocene", has been established by X-ray diffraction. This structure does indeed resemble that of the bisniobocene (XIV) and differs from it by the absence of two hydride hydrogen atoms, whose place in the molecule of compound (XXII) is taken by three electron pairs. The same compound has been obtained also from other isomeric bismolybdenocenes by their photochemical dehydrogenation.[111,113] It was found that all the reactions leading to compound (XXII) are extremely sensitive to a series of factors and their successful occurrence is strongly influenced by the temperature, the nature of the solvent, and the presence of specific nucleophilic additives (organic phosphines, etc.).

Two types of reactions have been carried out for the dehydromolybdenocene (XXII)—the complete cleavage of the dinuclear structure and oxidative degradation of the Mo–Mo σ-bond.[112-113] The latter reaction leads to the dinuclear complexes (XXIII), which are analogues of bismolybdenocene (XIX). It has been shown that the same compounds (XXIII) can be obtained directly from the molybdenocene (XIX) by treatment with the appropriate reagents under mild conditions:[108]




(XXIII)

XY=MeBr; MeI; $I_2$.

The complex (XXIII), in which the neopentyl substituents $CH_2CMe_3$ are σ-bound by the Mo–X and Mo–Y groups, was unexpectedly obtained by the reaction of $Cp_2MoCl_2$ with $LiCH_2CMe_3$.[114]

We shall now consider data on the dinuclear fulvalene complexes. As happens for the derivatives of Group IV and V metals, the bismolybdenocenes (XIX) and (XX) with the bridging $\eta^5:\eta^1$-$C_5H_4$ ligands enter comparatively readily into thermal reactions, rearranging under these conditions into bimetallic fulvalene derivatives. The simultaneous replacement of hydride hydrogen atoms by other more electronegative atoms accelerates these reactions significantly, enabling many of them to take place rapidly even at room temperature.

It has been noted that two types of bismolybdenocene complexes are formed.[101,106,108,110-112,115,116] Compounds of the first type [(X)(Y)CpMo($\eta^5$-$C_5H_4$-$\eta^5$-$C_5H_4$)MoCp(Y)(X)] (XXIV) are usually produced. The corresponding monometallocene analogues $Cp_2Mo$ (X)(Y) are known and have been thoroughly investigated for all the complexes (XXIV) synthesised. The chemical and physical properties of the mononuclear and dinuclear complexes are extremely similar owing to the absence of the mutual influence of the two metallic centres in compound (XXIV). In view of the foregoing, there is no point in considering in detail the reactions of compound (XXV). Another situation arises as regards the fulvalene bismolybdenocene complexes of the second type—compounds (XXV). These complexes have no direct analogues among the mononuclear derivatives. A distinctive structural characteristic of the molecule of compound (XXV) is the presence of the direct metal–metal bond, as a consequence of which the number of σ-bound groups is reduced by two in these compounds compared with compound (XXIV). The schematic formula (X)CpMo($\eta^5$-$C_5H_4$-$\eta^5$-$C_5H_4$)MoCp(X) corresponds to compounds (XXV); the groups X always occupy the terminal positions and cannot pass to the bridging positions owing to the electronic and coordination saturation of the metallic centres.

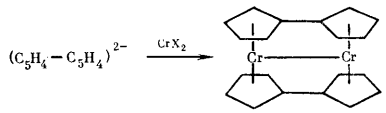
Certain reactions involving the Mo–Mo σ-bonds in the complexes (XXV) have been investigated and it has been shown that these reactions do not differ essentially from those which occur normally for different dinuclear complexes of other transition metals of the type $L_nM-ML_n$ without bridging groups. All the reactions in which compounds (XIX) and (XX) are converted into the fulvalene derivatives (XXIV) (XXV) and the principal reactions of the latter are indicated in the Scheme below.

The photochemical reactions of the fulvalenebismolybdenocenes, which permit the reverse conversion of the fulvalene complexes into compounds with bridging $\eta^5:\eta^1$-$C_5H_4$ ligands, are much more important and interesting. Such reactions have not been investigated at all for other dinuclear metallocene compounds.

It has been established that the photolysis of the fulvalene derivative (XXV) takes place rapidly in toluene in the presence of small amounts of added tri-n-propylphosphine, which results in a mixture of the *cis*- and *trans*-isomeric complexes (XIX).[113] It has also been observed that, in the presence of free phosphine, compounds (XXV) and (XIX) are virtually unable to be converted into the "dehydromolybdenocene" (XXII). At the same time the complex (XXII) is readily formed from both compound (XXV) and compound (XIX) by their photolysis in the absence of phosphine in the reaction mixture.[112] The mechanisms of these reactions are at present obscure. It has been suggested that intermediates containing both hydride hydrogen atoms at one metal atom, i.e. incorporating the $MoH_2$ fragment, lead to the "dehydromolybdenocene" (XXII). On the other hand, the role of phosphine in this process reduces to the fact that, by occupying coordination sites at the Mo atoms (and possibly also by converting some of the $\eta^5$-Cp ligands into $\eta^3$-bound ligands), it prevents the transfer of hydride atoms and the formation of intermediates with $MoH_2$ fragments.[112,113]

In conclusion we shall consider the very small amount of data on compounds containing two fulvalene ligands. As for vanadium (see above), the presence of two rigid polydentate ligands sharply restricts the capacity of such compounds for chemical reactions. The only bismetallocene complex of chromium, namely difulvalenedichromium, has been obtained by direct synthesis from the fulvalene ligand and a chromium

salt:[99]

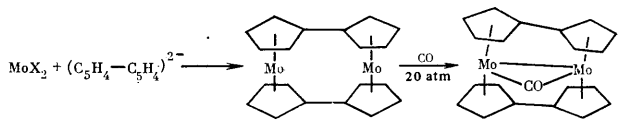


(XXVI)

Only one reaction of the complex (XXVI) has been achieved, namely oxidation leading to the formation of the corresponding monocation and dication.

The magnetic and spectroscopic characteristics of compound (XXVI) agree with the hypothesis of the direct overlap of the AO of the metal atoms, which results in the complete pairing of the electron spins in the ground state (even at temperatures below −50 °C). On the other hand, with increase of temperature, the excited paramagnetic states of the molecule are populated.[99]

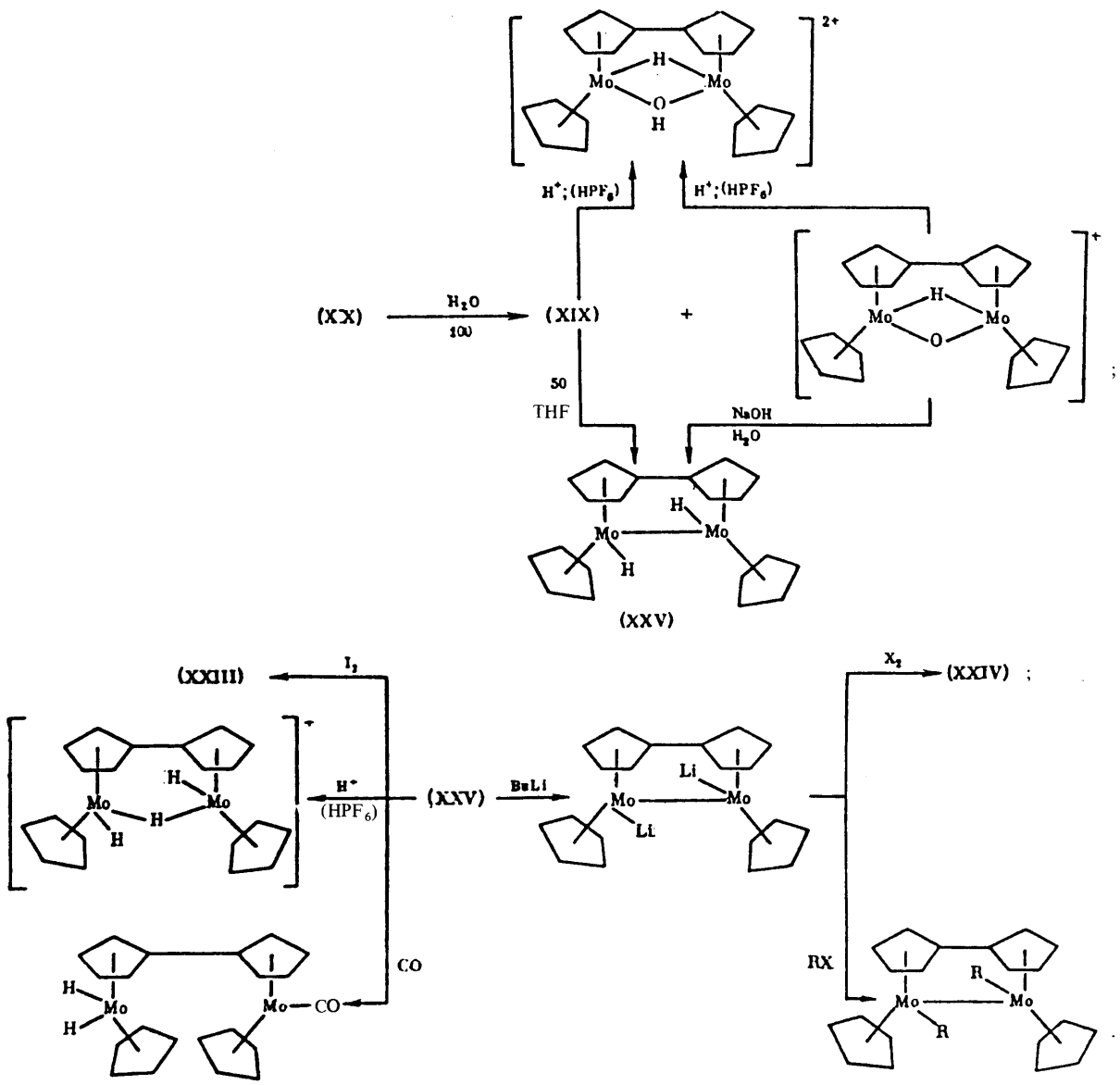
An analogous difulvalene complex has been synthesised for molybdenum [compound (XXVII)]; this is so far the only difulvalene derivative obtained for metals of the second transition series:[100]



(XXVII) (XXVIII)

The ready addition of carbon monoxide to compound (XXVII), which results in the formation of compound (XXVIII), can be easily explained by taking into account the coordination capacity of molybdenum and the entire data presented above. The question of metal–metal interaction in compounds (XXVII) and (XXVIII) has not been analysed in detail, but one cannot rule out the possibility that a multiple

Scheme



metal–metal bond exists in the molecule of compound (XXVII), since in the related complex tetraallyldimolybdenum a quadruple metal–metal bond is believed to be produced.[117]

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During the preparation of the manuscript for the press, one of the authors of this review obtained new data on the structure and reactions of the bisniobocene and bistitanocene complexes.[118–121] It was established that the replacement of one of the terminal hydride atoms in the bisniobocene (XIV) under mild conditions by a halogen atom entails the formation of thermally extremely unstable derivatives having apparently the structure $Cp(H)Nb(\mu\text{-}C_5H_4)_2NbCp(Hal)$. These intermediates rapidly rearrange to the thermally stable fulvalene hydride halide complexes $\mu\text{-}(\eta^5:\eta^5\text{-}C_{10}H_8)Cp_2Nb_2(\mu\text{-}H)(\mu\text{-}Hal)$ (XXIX), such rearrangements being both thermodynamically and kinetically allowed.[118,119] The bridging halogen atom in compound (XXIX) can be readily substituted by nucleophiles. The alkoxide hydride complexes $\mu\text{-}(\eta^5:\eta^5\text{-}C_{10}H_8)Cp_2Nb_2.(\mu\text{-}H)(\mu\text{-}OR)$ (XXX), where R = Me or Et, and the dihydride complex $\mu\text{-}(\eta^5:\eta^5\text{-}C_{10}H_8)Cp_2Nb_2(\mu\text{-}H)_2$ (XXXI) have been obtained in this way. The latter is an isomer of the bisniobocene (XIV). One cannot rule out the possibility that the majority of the syntheses of the stable isomer bistitanocene (V) described in the literature also proceed via the hydride halide fulvalene complex $\mu\text{-}(\eta^5:\eta^5\text{-}C_{10}H_8)Cp_2Ti_2(\mu\text{-}H)(\mu\text{-}Hal)$ (XXXII), by-passing the stage involving the formation of the metastable bistitanocenes. This conclusion agrees with the finding that the metastable bistitanocenes are converted into compound (V) usually under more severe conditions and that the yields of compound (V) are far from quantitative.

Compounds (XXX, R = Et) and (XXXII) have been studied by X-ray diffraction. Despite the different electronic configurations of the metal atoms, the structures of the two complexes are almost identical; the metal–metal distances are respectively $R$(Nb–Nb) = 3.136 Å and $R$(Ti–Ti) = 3.126 Å.[120]

The temperature variation of the $^1$H NMR spectra of compounds (V) and (XXXI) have been investigated.[121] The complex (XXXI) is diamagnetic, while the complex (V) is also diamagnetic at a low temperature (–60 °C) but at higher temperatures its excited triplet state is appreciably populated, which is manifested by the corresponding shift of the signals and broadening of the lines.

Mention should also be made of the study[122] of the rheniocene dimers. $(Cp_2Re)_2$ was obtained by oxidising $Cp_2ReLi$ with benzaldehyde. This complex gives rise to a single signal in the $^1$H NMR spectrum and is apparently associated only via a direct metal–metal bond. A disproportionation reaction is induced when it is heated in acetonitrile, which entails the formation of a mixture of $Cp_2ReH$ and $\mu\text{-}(\eta^5:\eta^1\text{-}C_5H_4)_2Cp_2Re_2$. The photolysis of $(Cp_2Re)_2$ leads to the formation of $\mu\text{-}(\eta^5:\eta^1\text{-}C_5H_4)CpRe(\eta^4\text{-}C_5H_6)ReCp$.

In conclusion of the review, we may say that the studies of recent years have led to the discovery of a large new field of bismetallocene complexes of the elements at the beginning of the transition series, the complexes having specific structures. Interesting many-centre rearrangements and certain unusual reactions have been observed for these complexes. The very fact of the formation of bismetallocenes demonstrates that the labile intermediates arising in the course of the reactions activate the C–H bonds of the organic ligands very effectively. On the other hand, the determination of the characteristic features of the electronic structures of the bismetallocenes already makes it possible not only to explain the experimental results but also to plan specific syntheses of quite definite new compounds.

However, it is evident that the point on which research is concentrated is beginning to shift. In the next few years there will probably be an appreciable expansion of research into the chemical properties of bismetallocenes and among them compounds of interest for practical applications will be found. The synthesis of mixed metallic complexes, whose chemistry is richer still, is also in the pipeline.

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# Sterols as Complex-forming Species

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The formation of complexes of sterols with different compounds determines the biological properties of both sterols and various natural substances such as saponins and polyene antibiotics. Complex formation by sterols with phospholipids, steroid saponins, and polyene antibiotics is determined by the same characteristic features of the structure of the sterol molecule. The principal role in complex formation is played by the hydrophobic reaction of the cyclopentanoperhydrophenanthrene ring. The formation of a hydrogen bond between the hydroxyl group of the sterol and a proton acceptor, which is assumed in most complexes, has been proved only in the complexes of sterols with water and acids.
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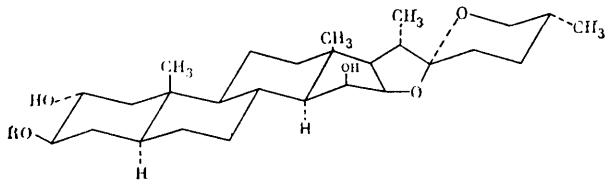
## I. INTRODUCTION

The ability of sterols in general and cholesterol in particular to form complexes† with steroid saponins was detected much earlier than the determination of the structural formula of cholesterol.[2] Since then, a large number of studies have shown that sterols form complexes with a number of organic compounds: alcohols, phenols, acids and their derivatives, amines, carbohydrates, various heterocyclic compounds, and recently proteins, and also with inorganic acids and salts. Complex formation with saponins has found extensive practical application in the preparative and analytical chemistry of sterols,[3,4] and complex formation with salts and alcohols is used to separate and purify sterols.[5,6] The formation of complexes of sterols with saponins forms the basis of the use of the latter as hypocholesterolemic agents,[7,8] and in recent years it has been used to develop sorbents which selectively extract the cholesterol of blood plasma.[9-11] However, it is not so much these applied aspects that are attracting interest in the complexes of sterols as the fact that complex formation determines a large part of the biological functions of sterols. Thus it was established at an early date that the biological action of polyene antibiotics is determined by the fact that they form complexes with membrane sterols. The same or a similar reaction explains the action of various toxins, for example tetrodotoxin and saxitoxin,[12] and also the membranotropic action of triterpene glycosides.[13] The incorporation of sterols into biological membranes takes place as a result of the formation of complexes with other components of the membranes, primarily phospholipids. Finally, in recent years there has been considerable interest in the reaction of sterols with proteins in lipoproteins, lipid–protein complexes which brind about the transport of lipids in living organisms.

The aim of the present work was to systematise individual scattered data on complex formation by sterols with various compounds, and to try to determine which intermolecular interactions are responsible for the high complex-forming power of sterols and which structural functions of their molecules are involved in these interactions. It should be stated at once that there are few published data on the quantitative study of sterol complexes. The published papers generally give no information on the stability constants of the complexes, their energies of formation, etc. Thus the present review is also based chiefly on qualitative relationships between the structure of sterols and their ability to form complexes.

## II. COMPLEXES WITH STEROID SAPONINS

In 1909, Windaus[2] found that cholesterol forms a sparingly soluble complex with digitonin, a steroid saponin (Ia). Complexes of this kind, which are called digitonides and which contain equimolar quantities of digitonin and a sterol, have been obtained for a whole series of sterols, and the solubility of the digitonides of different sterols depends on the nature of the latter These differences in the stability of the complexes have been widely used to separate sterols with similar structures, particularly epimers.




a) R = Xyl—Glc—Gal—
Gal—Glc

b) R = Xyl—Glc—Gal—
Gal

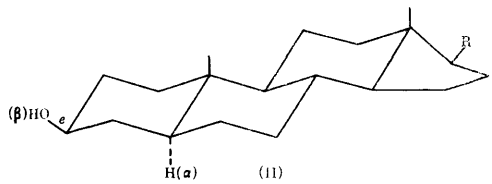
c) R = Glc—Gal—

Xyl = xylose, Glc = glucose, Gal = galactose

In the course of these studies, data were accumulated, relating the structure of a sterol to its ability to form a complex with digitonin. It should be emphasised, however,

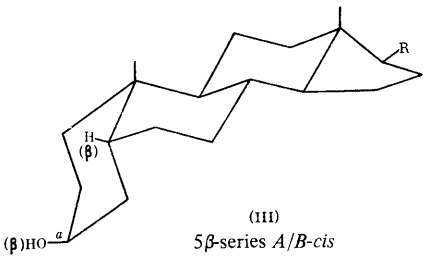
†According to Ref.1, the term "complex" signifies a molecular unit formed by the association of two compounds without change in the nature of the bonds within each part.

that the classification into sterols precipitated by digitonin and sterols not precipitated, frequently encountered in the literature, is extremely relative. The formation of a complex with digitonin is not determined entirely by the structure of the sterol; the dissociation of the complex is determined to a large extent by the reaction conditions, and in particular by the solvent and temperature. Thus digitonides have the minimum solubility in ethanol, in which they are prepared, but dissociate completely in such solvents as pyridine, dimethylformamide, and dimethyl sulphoxide.[14] The complexes dissociate when studied by chromatography on silica gel[15] and with increase in temperature; when cholesterol digitonide is heated in a vacuum to 240°, the cholesterol distils off practically completely.[16] Thus generalisations relating the stability of digitonides to the structure of sterols must be based on experiments carried out under rigorously comparable conditions, and there have been few such studies; the aim of most published work has been the preparative separation of isomers. Only a few authors[17–19] have determined quantitative characteristics of the stability of the digitonides of different sterols, namely the solubility product $S$. It is suggested that the lower the solubility and the value of $S$, the greater the ability of the sterol to form a complex. The data in Table 1 show that the lowest solubilities correspond to the digitonides of 3β-hydroxyl derivatives of the 5α-gonane series (II), that is compounds with *trans*-connection of the *A* and *B* rings, and also the corresponding $\Delta^5$-derivatives. All these compounds have a more planar molecule, compared with the 5β-conformers (III) and the 3β-configuration of the hydroxyl group:




(II)

5α-series *A/B-trans*




(III)

5β-series *A/B-cis*

| | |
|---|---|
| R=H | androstane |
| R=$C_nH_5$ | pregnane |
| R=CH $(CH_3)$ $(CH_2)_2CH_3$ | cholane |
| R=CH $(CH_3)$ $(CH_2)_3CH$ $(CH_3)_2$ | cholestane |

*a*—OH-group in the axial position, *e*—OH-group in the equatorial position.

The 3β-hydroxyl group plays a decisive role in the formation of the complexes; its acylation leads to a sharp increase in the dissociation of the complex, and this forms the basis of one method for separating sterols from digitonides. Not only acylation, elimination (separation or reduction), or oxidation at the keto-group, however, but even epimerisation of the 3β-hydroxyl group has a marked influence on the stability of the complexes. All 3α-hydroxy-derivatives of the 5α-series form complexes with S > 1100 × $10^{-8}$ mole$^2$ litre$^{-2}$, that is they are much more soluble than the 3β-derivatives.

**Table 1.** Influence of the structure of the sterol on the solubility of the digitonide.[17–19]

| Compound | Configuration of the 3-OH-group | | $10^8$ *S*, mole$^2$litre$^{-2}$ |
|---|---|---|---|
| 5α-Cholestan-3β-ol | β | *e* | 4 |
| 5α-Cholestan-3α-ol (epicholestanol) | α | *a* | 2200 (900) |
| 3β-Acetoxy-5α-cholestane | β | *e* | 1100 |
| Cholest-5-en-3β-ol (cholesterol) | β | *e* | 4 |
| 3β-Acetoxycholest-5-ene | β | *e* | >1100 |
| 5β-Cholestan-3β-ol (coprostanol) | β | *a* | 70 |
| 5β-Cholestan-3α-ol (epicoprostanol) | α | *e* | 2200 |
| Stigmasta-7,22-dien-3β-ol (stigmasterol) | β | *e* | 4 |
| 5α-Ergost-7,22-dien-3β-ol (ergosterol) | β | *e* | 4 |
| Methyl 3β-hydroxy-5α-androstan-17-carboxylate | β | *e* | 8 |
| Methyl 3β-hydroxy-5β-androstan-17-carboxylate | β | *a* | >2200 |
| 5α-Pregnan-3β, 20β-diol | β | *e* | 140 |
| 5β-Pregnan-3β, 20β-diol | β | *a* | >1100 |
| 5α-Pregnan-20-keto-3β-ol | β | *e* | 4 |
| 5β-Pregnan-20-keto-3β-ol | β | *a* | 1100 |
| Pregn-5-en-20-keto-3β-ol | β | *e* | 4 |
| 5α-Androstan-3β-ol | β | *e* | 8 |
| 5-Androsten-3β-ol | β | *e* | 35 |
| 5α-Androstan-17-keto-3β-ol | β | *e* | 140 |
| 5α-Androstan-17-keto-3α-ol | α | *a* | 2200 |
| 5β-Androstan-17-keto-3β-ol | β | *a* | 1100 |
| 3α-Methyl-5α-androstan-3β-ol | β | *e* | 35 |
| 3β-Methyl-5α-androstan-3α-ol | α | *a* | 1100 |
| 5α, 22-Spirostan-3β-ol (tigogenin) | β | *e* | 70 (16) |
| 5β, 22-Spirostan-3β-ol (sarsapogenin) | β | *a* | 280 (970) |
| Cholest-4-en-3-one | | | >2200 |

The difference in the reactivities of epimers of sterols with different conformations of the 3-hydroxyl group is well known. Equatorial hydroxyl groups are less shielded than axial groups, so that they undergo certain reactions more readily. For example, they are more readily acylated, and the corresponding esters are more readily hydrolysed. Epimers with an equatorial hydroxyl group are more strongly sorbed on various carriers, indicating that they form more stable complexes,[20,21] possibly by hydrogen bonding.[22] It is logical to assume that the differences in the ability of epimeric sterols to form digitonides is also related to the equatorial or axial arrangement of the 3-hydroxyl groups. It has been suggested, however, that in complex formation with digitonin, the decisive role is played not by the equatorial or axial arrangement of the 3-hydroxyl groups but by their α- or β-arrangement relative to the cyclic system.[3,23] This generalisation appears unjustified. It can be seen from Table 1 that among epimeric compounds, the lower solubility is shown by the equatorial 3-isomer, irrespective of the position, α or β, occupied by the 3-hydroxyl group in the axial epimer#. An exception is provided by coprostanol and epicoprostanol, for which the opposite relationship is observed. It was on the basis of this pair of compounds that the suggestion that the α- or β-arrangement of the hydroxyl group plays a decisive role in the formation of digitonides was first put forward, and it was subsequently repeated in the literature, in spite of the large number of exceptions. It should be emphasised that for most of these exceptions, that is when the compound with the 3β-hydroxyl group does not form a digitonide, the hydroxyl group occupies the axial position (lumisterol, the methyl esters of 3β,5β,14β-trihydroxyandrostan-17β-carboxylic acid and its 17α-epimer, methyl 3β-hydroxy-11α-acetoxy-

#In the 5α-gonane series, the 3β-hydroxyl group is equatorial, and the 3α-group is axial, whereas in the 5β-gonane series, the 3β-hydroxyl group is axial, and the 3α-group is equatorial.

5β-androstan-17β-carboxylate, and the cardenolide aglycones gitoxigenin, digitoxigenin, sarmentogenin, and strophanthidin).[4,24] Moreover, in individual cases it has been shown that the corresponding 3α-epimer, whose hydroxyl group is equatorial, forms a digitonide, in contrast to the 3β-axial epimer (epilumisterol).[25] All this indicates that the influence of the 3-hydroxyl group in the formation of complexes with digitonin is determined not by its α- or β-arrangement but by its equatorial or axial arrangement, and is related to the same steric factors as the above differences in reactivity. This suggestion naturally requires confirmation using a larger amount of experimental material than is available at present.

The lower complex-forming power of the axial epimers is not the only feature illustrating the influence of steric factors on the formation of digitonides. Thus the introduction of an additional methyl group into a sterol in position 3 makes the formation of the digitonide more difficult, while the relationship between the stabilities of the equatorial and axial epimers is preserved (see Table 1). The introduction of additional methyl groups in position 4 of the molecule on going from cholesterol to lanosterol also leads to higher solubility of the digitonide.[26] Esters of 3β-hydroxyandrostan-17-carboxylic acid, containing the bulky diphenylmethane group in the alcohol fraction of the molecule, also do not form digitonides, in contrast to the esters with simple alcohols (methanol, ethanol).[24]

The role of the aliphatic chain on the C(17) atom in the formation of sterol digitonides has been less extensively studied than the role of the hydroxyl group. The data in Table 1 show that the double bonds in the aliphatic chain of ergosterol and stigmasterol have no influence on the stability of the complex, whereas in the series of identical derivatives of cholestane, cholane, pregnane, and androstane, decrease in the length of the chain leads to a slight but regular decrease in the stability of the digitonide. The competitive formation of digitonides by cholesterol and its synthetic analogues containing unbranched aliphatic chains of different length on the C(17) atom has been studied.[27] Gradual increase in the length of the chain increases the stability of the complex, which became equal to the stability of cholesterol digitonide for the compounds containing 8–10 carbon atoms in the side chain. Further increase in the length of the aliphatic chain to $C_{11}$–$C_{13}$ gave digitonides with an even higher stability, but at $C_{15}$ the stability of the complex decreased sharply.

In addition to the dependence of complex formation on the structure of the sterol, some data have been published on the influence of the structure of the second component of the complex, that is the saponin, on this process. Complexes with sterols are formed not only by digitonin but also by a whole series of steroid saponins, and also various steroid alkaloids[20,28] and triterpene glycosides.[13] Comparison of the stability of the complex with the saponin aglycone structure indicates that spirostanol saponins containing six rings form less soluble complexes than furostanol saponins, which contain one fewer ring.[9,29,30] The structure of the glucoside residue of the saponin has a marked influence on complex formation. The optimum number of monose residues for complex formation is 4–5, and decrease in this number leads to an increase in the solubility of the complexes.[9,10,30] A quantitative study has shown that desglucosodigitonin (*Ib*), which contains four monose residues, has practically the same complex-forming power as digitonin (*Ia*), whereas glucosogalactosodigitonin (*Ic*), obtained by removing three monoses from natural digitonin, does not form a complex with cholesterol under the conditions studied.[27]

The above regular features relating the stability of the complex to the structures of both the sterol and the saponin have made it possible to put forward suggestions about the structure of the complex itself.[27] It is suggested that the digitonide is a clathrate, in which the saponin is the host, and the sterol the guest. The digitonin molecules are oriented to form a hydrophobic cabity capable of accommodating a guest molecule. This model assumes that the aglycone fraction of the saponin undergoes a hydrophobic interaction with the sterol molecule. The rigid cyclic systems of the two components ensure that the interaction is equimolar. A mobile aliphatic side chain on the C(17) atom of the guest molecule, capable of changing its position in space and undergoing an additional hydrophobic interaction with the host molecule, should, for a definite length, ensure stability of the complex. In a development of this hypothesis it may be assumed that the part of the host cavity which is formed by the glucoside residue and which is hydrophilic in character leads to stabilisation of the complex as a result of the formation of hydrogen bonds between the hydroxyl groups of the sugars and the 3-hydroxyl group of the sterol. This last suggestion agrees with the stability of the digitonides of steroids which contain in position 3 not a hydroxyl group but certain other groups capable of acting as proton donors or acceptors in hydrogen bond formation, such as amino- or dimethylamino-groups,[4,31] but not the thiol group,[32] which is a less effective partner in hydrogen bond formation. The hypothesis is supported by other factors. The ability of cholic acids to act as the host in clathrates with various compounds, including cholesterol, is well known.[33] The common features of the structures of saponins and cholic acids include not only the common hydrophobic cyclopentanoperhydrophenanthrene framework, but also the necessary presence of hydrophilic groups—the carboxyl group in cholic acid, and the hydroxyl groups of the sugars in the saponins. The blocking or elimination of these groups by esterification of the acid or the removal of monoses makes the compounds unable to form complexes.

Steroid saponins have a marked haemolytic and antimycosal action. The dependence of these properties on the chemical structure of the saponins shows regular features analogous to those of the above relationships between the complex-forming power and the structure. For example, the maximum haemolytic activity is shown by spirostanol saponins containing 4–5 monose residues.[34,35] This parallel suggests that the haemolytic action of saponins and other glycosides is due to complex formation with membrane sterols.[36,37,38] and this increases the interest in the complexes of sterols with saponins.

## III. STEROL CRYSTALLINE SOLVATES

Only a few papers have been published on these sterol complexes. The crystalline hydrates of cholesterol, formed by crystallising the latter from aqueous solvents (alcohol, acetone), gradually lose water of crystallisation at ordinary temperatures, and are completely dehydrated at 80°.[39,40] The crystalline hydrates of other sterols such as β-sitosterol and ergosterol behave similarly. Sterols also form complexes with alcohols[41] and inorganic and organic acids, the highest stability being shown by the complexes with the strong acids perchloric,[42] trichloroacetic,[43] and oxalic.[44]

It is logical to assume that in complex formation by a sterol with small polar molecules, the hydrophobic inter-

action between them plays an insignificant role, and that the principal contribution is made by forces associated with the hydroxyl group. Thus only sterols with a free 3β-hydroxyl group, and not sterol esters, form both crystalline hydrates and complexes with acids. Similarly, the corresponding complexes are not formed by compounds which do not contain hydroxyl groups, such as cholestenes and cholestadienes. It has been shown qualitatively that, as in the formation of digitonides, a decisive role in complex formation with perchloric and oxalic acids is played by not only the presence but also the configuration of the 3-hydroxyl group. Thus unlike 5α-cholestan-3β-ol and cholesterol, the corresponding 3α-epimers do not form oxalates or perchlorates.[42,44]

In contrast to digitonides, where hydrogen bonding has only been assumed, in the case of the crystalline solvates various data have been published on the nature of the hydrogen bond between the hydroxyl group of the sterol and the second component of the complex.

In the crystal of cholesterol[45] and its esters containing a polar group in position 3, such as the hydrogen sulphate[46] and phosphate,[47] the molecules are packed in structures in which the rigid system of rings, the substituent on the C(3) atom, and the aliphatic side chain are arranged in different positions in the molecular layer. Within the layer, the molecules are arranged in two series with their planar rear α-sides turned towards one another, favouring the maximum hydrophobic interaction. On the other hand, neighbouring double bonds make contact through their frontal β-sides. The double layers are displaced slightly (~0.85 Å) relative to one another in such a way that the angular methyl groups projecting above the surface are entangled. The maximum hydrophobic interaction is achieved when the long axes of the molecules are parallel, but at the same time this parallel arrangement leads to an increase in the distance between the oxygen atoms of the two hydroxyl groups of two molecules of the bilayer, to a value >3.0 Å, preventing the formation of a hydrogen bond between them. On the other hand, when the two hydroxyl groups approach one another to a distance <2.5 Å to give a strong hydrogen bond, the parallel arrangement of the molecules breaks down, and the hydrophobic interaction decreases. Thus in the cholesterol crystal there is a compromise between these two requirements: the parallel arrangement of the axes of the molecules is slightly disturbed, and the O...O distance is 2.87 Å, which is at the upper limit for possible hydrogen bond formation. In cholesterol monohydrate, however, hydrogen bond formation takes place not between two cholesterol hydroxyl groups but through water molecules acting as bridges.[48,49] This makes it possible for two cholesterol molecules to be joined by a hydrogen bond while preserving the parallel arrangement of the axes of the molecules. Thus in the crystal of cholesterol monohydrate there is a greater interaction between the individual parts of the two molecules than in the crystal of the anhydrous substance, that is the inclusion of water in the polar fraction of the molecules also increases the strength of the hydrophobic interaction.

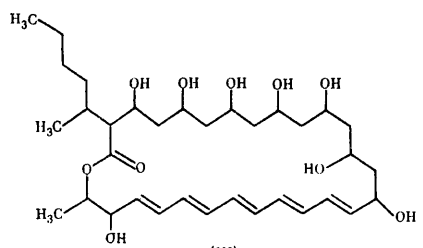
Complex formation by cholesterol with other ligands, for example acids, apparently takes place similarly. Infrared spectroscopy has shown that the reaction of cholesterol with trichloroacetic acid in carbon tetrachloride solution involves the formation between them of a hydrogen bond, in which the acid acts as proton donor, and cholesterol as proton acceptor.[50] Increase in the concentration of both components leads to aggregation of the binary particles as a result of the formation of new hydrogen bonds between them. In these aggregates, the hydroxyl group of cholesterol acts simultaneously not only as a proton acceptor, but also as a proton donor, which accepts either the hydroxyl group or the carbonyl group of the acid. In the solid complex, the role of acceptor is apparently played only by the carbonyl group of the acid; in this case the bridge formed is longer, and creates more favourable conditions for the interaction of two sterol molecules in the crystal.

The proposed model requires that not only cholesterol but also the second component of the complex should be not only a proton acceptor but also a proton donor in hydrogen bond formation. Thus cholesterol forms solid complexes with alcohols, but not with esters, and only with those amides which contain $NH_2$ or NHR groups.[50]

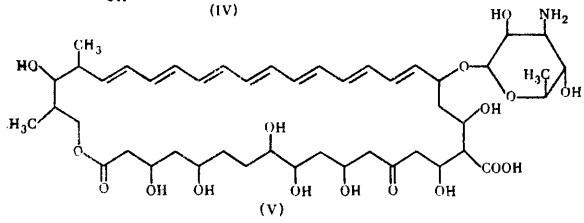
Cholesterol and other sterols form complexes with various salts, for example chlorides.[6,51] Published data on these complexes are few and often contradictory, but the hydroxyl group plays an important role in their formation. Thus only compounds with a free 3β-hydroxyl group, and not sterol esters or 3α-epicholesterol, form complexes with calcium chloride.[52] The rate of acetylation of the hydroxyl group of cholesterol in its complexes with calcium and magnesium chlorides is higher than the rate of acetylation of the sterol itself.[53] The complexes with salts also apparently contain water molecules, as confirmed in a number of cases by analysis.[6,52] The conditions of preparation of other complexes with salts also indicate that they contain water molecules, but unfortunately, no analytical data are available.

## IV. COMPLEXES WITH POLYENE ANTIBIOTICS

The biological action of polyene antibiotics is due to their complex formation with the sterols of cell membranes. The proof of this mechanism and the investigation of the relationship between the structure and action of antibiotics have been the subject of a large number of publications, including a number of reviews,[54-58] so that the present review will only list briefly the characteristic features of the structure of polyene antibiotics, for example filipin (IV) and amphotericin B (V). Polyene antibiotics are characterised by the presence of a macrolide ring, formed by the closure of a lactone ring. One side of the ring consists of a system of 4–7 conjugated double bonds. The total number of carbon atoms in the ring is $4n + 4$, where $n$ is the number of double bonds of the polyene chain. A second characteristic feature is the large number of hydroxyl groups, from 6 to 14, situated on the opposite side of the ring. Finally, most polyene antibiotics contain a mycosamine residue.



(IV)



(V)

The simultaneous presence in the molecule of a polar region, formed by a number of hydroxyl groups, and a rigid hydrophobic system of conjugated double bonds is responsible for the amphipathic properties of polyene antibiotics, for example their ability to form micellar solutions. It follows from the above material that this amphipathic character may be responsible for the ability to form complexes with sterols. Unlike the crystalline complexes described above, the complexes of sterols with antibiotics have not been isolated in the crystalline state, and their formation has been demonstrated by various physicochemical methods, primarily spectroscopic methods. The addition of sterols to solutions of polyene antibiotics produces a characteristic change in the ultraviolet spectra of the latter, namely a change in the ratio of the absorptivities of different maxima, indicating that the antibiotic reacts with the sterol. Complex formation is reversible, and depends on the solvent and temperature. The change in the spectra of the antibiotics, measured by the ratio of the absorption at 320 nm and 356 nm (the so-called 1:3 peak ratio), takes place only in the reaction with the sterol. The data in Table 2 show that the addition of other compounds such as cetyl alcohol or lecithin to a filipin solution produces no change in the spectrum; the changes brought about by secosteroids are also very slight. The ability to form a complex with an antibiotic is also influenced by the presence of a 5α-gonane system, an aliphatic chain on the C(17) atom, and a 3-hydroxyl group on the C(3) atom, although there are also unexplained exceptions, namely the 3-ketoderivatives. More definite information can be obtained by comparing the changes produced in the spectrum of filipin by its reaction with not a free sterol but a sterol in a sterol–lecithin liposome. In the case of liposomes containing 16–50% sterol, the optimum interaction is observed for sterols containing a 5α-gonane or $\Delta^5$-gonene ring and a aliphatic chain on C(17). In this case, complex formation depends on the substituent on C(3). The maximum interaction is shown by compounds with a free 3β-hydroxyl group, and its acetylation, oxidation, or epimerisation leads to a sharp decrease in the stability of the complex. According to Ref.61, the dissociation constant of the epicholesterol–filipin complex is 15 times the corresponding constant of the cholesterol–filipin complex. Similar regular features are observed for sterols in not liposomes but natural membranes. A culture of Acholeplasma Laidlawii does not contain sterols in the cell membranes, but is capable of including them in the membrane when grown in sterol-containing media. This is widely used in the study of the influence of sterols on the properties of biological membranes.[62] It follows from the data in Table 2 that the reaction of filipin with this membrane also leads to characteristic changes in its ultraviolet spectrum. Maximum complex formation takes place in the case of membranes containing sterols of the 5α- or $\Delta^5$-series with a 3β-hydroxyl group; the spectral changes are much less marked on going to the 5β-series (coprosterol) and to the 3α-epimers (epicholesterol).

The dependence of complex formation with an antibiotic on the structure of the sterol is confirmed by not only ultraviolet but also fluorescence spectroscopy.[63] The formation of complexes with sterols leads to quenching of the fluorescence of the antibiotics. Data on the quenching of the fluorescence of antibiotics brought about by the formation of complexes with sterols show that complex formation with filipin, amphotericin, and pimaricin is a maximum for sterols containing a 3β-hydroxyl group, and that practically no complex formation takes place when this group is acylated or epimerised.[64] Similar results have been obtained in spectroscopic studies of the reactions of sterols with other polyene antibiotics. All these data indicate that the stability of the complexes of sterols with antibiotics is determined by the same characteristic features of the sterol structure as the stability of the complexes with saponins. The following model of the complex of an antibiotic with a sterol has been proposed by a number of authors.[65,66] When the antibiotic enters the membrane its hydrophobic polyene chain reacts with the hydrophobic cyclic system of the sterol to form a 1:1 complex. Several such complexes (eight in the case of amphotericin B) join together to form a so-called semi-pore, whose inner part, containing a large number of hydroxyl groups, acts as a hydrophilic canal. Two semi-pores form a pore penetrating the membrane. The hydroxyl group of the sterol and the polar amino- and carboxyl groups of amphotericin B are on the membrane surface facing water. It is assumed that hydrogen bond formation between these groups is possible.

Table 2. Influence of the structure of the sterol on complex formation with philipine (3:7 peak ratio in the ultraviolet spectrum).

| Compound | In aqueous solution (Ref.59) | In liposomes (Ref.59)* | In natural membranes (Ref.60) |
|---|---|---|---|
| Original solution | 0.72 | — — | — |
| 5α-Cholestan-3β-ol | 2.17 | 1.35; 1.94 | 2.99 |
| 5α-Cholestan-3α-ol | — | — — | 1.16 |
| Cholest-5-en-3β-ol | 2.12 | 1.40; 1.95 | 2.18 |
| Cholest-5-en-3α-ol | 1.63 | 0.85; 1.04 | 1.47 |
| 3β-Palmitoylcholest-5-ene | 1.78 | — — | — |
| 5β-Cholestan-3β-ol | 1.56 | 0.88 — | 1.35 |
| Stigmasterol | 1.70 | 1.71; 2.23 | 1.56 |
| Ergosterol | 1.88 | 1.48; 1.70 | 2.01 |
| 5α-Androstan-3β-ol | 1.52 | 0.94; — | — |
| 5α-Androstan-3α-ol | 1.50 | — — | — |
| Cholest-5-en-3-one | 2.50 | — — | — |
| 5α-Cholestan-3-one | 2.27 | 0.90; 0.96 | — |
| Dihydrotachysterol | 0.92 | — — | — |
| Vitamin $D_2$ | 0.84 | — — | — |
| Lecithin | 0.88 | — — | — |
| Cetyl alcohol | 0.78 | 0.87; — | — |

*First figure—16% sterol, second figure—50% sterol.

The change in the penetrability of natural membranes brought about by the addition of antibiotics is determined by the nature of the sterol present in the membrane.[54] The maximum change is observed when cholestanol and cholesterol are present, whereas their epimers undergo practically no reaction with antibiotics. The need for the presence of a 3β-hydroxyl group for the reaction with an antibiotic was also proved in a study of the conductivity of bimolecular lipid membranes; the addition of levorin increased the conductivity of membranes containing cholesterol by a factor of $10^5$, but increased the conductivity of membranes containing esterified cholesterol and cholest-5-en-4-one by a factor of only 10.[67]

The proposed model of the sterol–antibiotic complex explains satisfactorily the role of the sterol framework. The planar polyene chain of the antibiotic molecule complements to a maximum extent the planar cyclic system of the sterol. Breakdown of the planarity of the polyene chain by the introduction of one simple bond (nystatin) or by the complete reduction of all the double bonds (hydrogenated amphotericin) reduces the complementarity of the interacting molecules.[68] An even greater influence on the

stability of the complex is shown by breakdown of the planarity of the cyclic system in secosteroids (see Table 2) or by the steric hindrance produced by geminal methyl groups in such sterols as tetrahymanol,[64] eburicol, and lichesterol.[69] On the other hand, an increase in the planarity of the sterol molecule facilitates complex formation (Table 2). This has been confirmed by studies of the conductivity of bilayer lipid membranes; the increase in the conductivity brought about by the addition of levorin is proportional to the number of double bonds in the sterol framework.[70,71] According to Ref.72, the complete aromatisation of the ring *A* of the sterol also favours complex formation with antibiotics.

Although it explains the role of the sterol framework in the hydrophobic interaction, the proposed model does not explain the importance of the aliphatic chain on C(17). The data in Table 2 show that androstane derivatives have a much lower complex-forming power than cholestane derivatives. A gradual decrease in the length of the side chain in synthetic homologues of chlolesterol also leads to a decrease in their ability to form complexes with antibiotics.[73] Another factor is the degree of branching of the side chain, as can be seen by comparing cholesterol, β-cytosterol, and stigmasterol. The introduction of double bonds not only into the rings but also into the aliphatic chain favours complex formation with antibiotics.[70,71] It should be noted, however, that the role of double bonds is different for complex formation with different antibiotics. Thus filipin forms a more stable complex with cholesterol than with ergosterol, but amphotericin, pimaricin, and nystatin form more stable complexes with ergosterol than with cholesterol.[74,78] The authors cited relate this difference to the presence of mycosamine in the structure of the last three antibiotics, but they leave open the question of how mycosamine can react with the additional double bonds in the ergosterol molecule. At the same time, this question is of not only theoretical but also applied importance; its solution facilitates the choice of particular antibiotics for treating different illnesses. The role of the 3β-hydroxyl group also remains unexplained. Although the formation of a hydrogen bond between the hydroxyl group of a sterol and the functional groups of antibiotics has been postulated repeatedly on the basis of the observed dependence of complex formation on the sterol structure, the existence of this bond has not been proved. A leading role in the formation of the sterol–antibiotic complex is apparently played by the hydrophobic interaction, particularly in solutions, where the solvent prevents hydrogen bond formation. The decisive role of the hydrophobic interaction in solutions is confirmed by the fact that complex formation is influenced by the presence of detergents and organic solvents, and is not influenced by the addition of salts and organic compounds.[78,79] In the reaction with a sterol in a membrane, the possibilities for hydrogen bond formation are greater, and this is revealed by the clearly defined influence of the nature and the sterochemistry of the substituent on C(3) on complex formation. Even in a membrane, however, the sterol–antibiotic interaction is weaker than the sterol–saponin interaction, as proved by the fact that digitonin blocks the action of antibiotics on membranes.[54] On the other hand, the fact that the antibiotic enters the membrane indicates that the interaction of the sterol with the antibiotic is stronger than the interaction of the sterol with other components of the membrane. It may also be noted that the reaction of cholesterol with levorin and amphotericin B inhibits the enzymatic esterification of cholesterol by lecithin–cholesterol–acetyltransferase.[80]

## V. STEROLS IN MEMBRANES

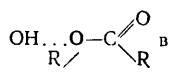
The role of cholesterol and other sterols in the structure of natural membranes and their models has been examined in detail in a number of reviews and monographs (see for example Refs.81–83). The sterol molecules are introduced between the hydrocarbon chains of phospholipids, and the intermolecular interaction between the sterol and the phospholipid is greater than the interaction between identical molecules of both phospholipids and sterols. The main structural function of cholesterol in the membrane is to stabilise the hydrophobic part of the bilayer by decreasing the mobility of the hydrocarbon chains at temperatures above the phase transformation and increasing their mobility at temperatures below the phase transformation. Both the condensing and the decondensing ("liquefying") effects of sterols have been proved by various physical methods in natural and model membranes. This influence is determined to a large extent by the structure of the sterol.

Only compounds containing a 3β-hydroxyl group influence the properties of lecithin monolayers.[84,85] The 3-keto-steroids cholestan-3-one and its $\Delta^4$-, $\Delta^5$-, and $\Delta^{4,6}$-derivatives have a much weaker condensing effect and have practically no influence on the permeability of liposomes for glucose, glycerol, and the $Rb^+$ cation. The influence of the 3-hydroxyl group is determined by its conformation; the presence of 3α-epicholesterol has no influence on the permeability of the membranes of Acholeplasma Laidlawii for glycerol and erythritol or on the energy of the phase transformation in these membranes.[86] As in the case of the complexes of sterols with saponins and antibiotics, the specific role of the 3β-hydroxyl group has been explained by assuming that a hydrogen bond is formed between this group and some acceptor group of the phospholipid. It was first suggested that the phosphate group acts as proton acceptor, but this suggestion was rejected on the basis of $^{31}P$ NMR data.[87,88] At almost the same time it was shown that the sterol is arranged in the lipid bilayer in such a way that its hydroxyl group is located close to the glycerol residue of the phospholipid.[89,90]§ This led to the appearance of several models of the hydrogen bond between the hydroxyl group of the sterol and the carbonyl group of the aliphatic acid of the phospholipid. The first of these postulates the existence of "hydrogen belts" in the membrane, including hydrogen bonds between hydrated cholesterol and the carbonyl group.[92] An examination of models of cholesterol and the phospholipid showed that the formation of a bond of this kind should lead to a stronger hydrophobic interaction with the hydrocarbon chain not only of the planar α-surface of the sterol but also of its β-surface, where the projecting angular methyl groups on C(10) and C(13) are inserted into a hydrophobic "loop" formed by the unsaturated aliphatic acid.[93] Although some studies by the authors of these hypotheses[94] indicated an OH...O=C bond, more detailed studies did not confirm its existence. It was shown that the influence of epicholesterol on the chemical shift of the signals in the NMR spectrum of dipalmitoyl-lecithin containing a $^{13}CO$-group is much greater than the corresponding influence of cholesterol.[95] At the same time it was suggested that it is cholesterol, and not its epimer, that forms a hydrogen bond with the carbonyl group. An infrared and Raman spectroscopic study of the carbonyl

§To counterbalance this, it has recently been shown[91] that the hydroxyl group of cholesterol is situated close to the phosphate group of lecithin.

absorption of the same phosphatidylcholine in the presence of cholesterol showed that there is no hydrogen bond between the hydroxyl and carbonyl groups, at least in the anhydrous specimens.[96] Some spectral changes in the carbonyl region of hydrated dipalmitoylphosphatidylcholine are observed, however, when cholesterol is added.[97] The Raman spectrum of anhydrous crystalline dipalmitoylphosphatidylcholine shows a carbonyl group doublet, corresponding to two different acyl groups in different conformations. Hydration of dipalmitoylphosphatidylcholine, which converts it into a gel phase, transforms this doublet into a single band, as a result of the formation of the conformationally uniform phospholipid. The addition of cholesterol to the hydrated phospholipid, however, splits the carbonyl band again, and it becomes similar to the doublet in the spectrum of the crystalline specimen. The two conformations of the acyl chains of phosphatidylcholine in the gel phase in the presence of cholesterol were also demonstrated by $^{2}H$ and $^{13}C$ NMR spectroscopy.[98,99] Compounds which cannot act as proton donors, such as the methyl ester of cholesterol, do not influence the conformation of the aliphatic acid chains. Thus the influence of cholesterol on the conformation of the acyl chains of the phospholipid indicates indirectly that a hydrogen bond is formed, but cannot prove the existence of the OH...O=C bond.

An attempt was recently made to resolve this contradiction. From a detailed examination of molecular models, it was suggested[100] that a hydrogen bond is formed between the hydroxyl group of cholesterol and the ester oxygen and not the carbonyl oxygen, of the alkoxycarbonyl group. Although the ester oxygen is a weaker proton acceptor than the carbonyl oxygen, it can fulfil this role when the steric arrangement is favourable.[101,102] Examination of molecular models shows that for the maximum hydrophobic interaction between the α-side of the sterol ring and the hydrocarbon chain of lecithin, the hydroxyl group of cholesterol is arranged in such a way that it can form a linear hydrogen bond with the ester oxygen, but not with the carbonyl oxygen. In the case of the α-conformation of the hydroxyl group (epicholesterol), however, this bond is impossible. The proposed hypothesis makes it possible to explain both the difference in the conformations of the two acyl chains in the presence of cholesterol and the difference in the influences of the cholesterol epimers on the properties of the lipid layers. It should be noted, however, that no experimental proof of the formation of an



bond was obtained in this case.

The question of hydrogen bond formation was investigated by another method, by studying the influence of cholesterol on the properties of model membranes constructed from different lipids. In one case the membranes consisted of lipids containing ester or ether groups capable of acting as proton acceptors in hydrogen bonding, and in the other case these groups were replaced by hydrocarbon chains incapable of acting as proton acceptors.[103-107] It was found that the addition of cholesterol to the last membranes, where hydrogen bond formation is impossible in principle, brings about the same condensing effect as in membranes containing ester and ether groups. It is true that it was shown for the first time that there is a slight difference in the changes in the permeability of membranes of different types under the influence of cholesterol,[104] but this difference was not confirmed in subsequent studies.[105-107]

Irrespective of whether a hydrogen bond is present or absent, the localisation of the hydroxyl group close to the glycerol residue of the phospholipid, confirmed by recent studies,[108,109] is responsible for the definite arrangement of cholesterol in the membrane. The gonane ring is fixed between the C(2) and C(8) atoms of the aliphatic acid, and it is the interaction in this section that determines the stability of the complex. As in the complexes with saponins and polyene antibiotics, the stability is determined primarily by the planar α-surface of the sterol. It was shown in Refs.84 and 85 that cholestanol, which is a planar sterol of the α-gonane series, has a more marked condensing effect and a stronger influence on the permeability of membranes, compared with coprostanol. An increase in the planarity of the cyclic system by the introduction of double bonds into the *B* ring (cholesterol, dehydrocholesterol) or by the replacement of the six-membered ring by a five-membered ring (*B*-norcholesterol) increases this influence. On the other hand, the introduction of methyl groups, which break down the planarity of the α-surface of the sterol, decreases its influence on the properties of membranes. The decrease is proportional to the number of these groups: cholesterol < 4α-methylcholesterol < 4,4-dimethylcholesterol < 4,4-diethylcholesterol ≪ 4,4,14α-trimethylcholesterol (lanosterol).[110] The influence of the three-dimensional structure of the sterol on other properties of the membrane, for example the micro-viscosity, is completely analogous.[111,112] An interesting feature is that the above sequence corresponds to the step wise demethylation of the precursors of cholesterol during its biosynthesis. The biological demethylation is highly selective, and only the α-surface of the sterol is affected. This creates a planar surface, capable of maximum interaction with the aliphatic chain of the phospholipid. At the same time, practically all natural sterols contain β-methyl groups on the C(18) and C(19) atoms. Apparently, elimination of these groups does not take place because this would not lead to an increase in the strength of the contact between the sterol and the phospholipid. Moreover, according to the hypothesis of Ref.93, the β-methyl groups are necessary for more complete contact with the unsaturated aliphatic chain.

The interaction between the aliphatic chain of the phospholipid and various sterols differing in the planarity of the α-surface was recently studied by the spin probe method, using stearic acid containing nitroxyl groups on the C(5), C(7), C(12), and C(17) carbon atoms.[113] As suggested, methyl groups situated on the α-surface bring about considerable perturbation of the EPR spectrum, and this perturbation is determined by the relative arrangement of the methyl groups of the sterol and the nitroxyl groups of the probe. The methyl group of 3α-methylcholesterol brings about considerable perturbation in the region of the C(5) atom of stearic acid and less perturbation in the region of C(7) and C(12). Lanosterol, on the other hand, brings about perturbation chiefly in the region of C(12), from its C(14) methyl group, and brings about less perturbation in the region of C(5) and C(7). All this indicates that there is considerable contact between the sterol molecules and the section of the aliphatic acid from C(2) to C(9), which is broken down by the projecting axial methyl groups. The compounds studied bring about practically no perturbation of the signal in the region of the C(17) carbon atom, indicating that there is little interaction between the isooctyl chain of the sterol and the aliphatic chain of the acid.

The side chain of the sterol plays a lesser role in complex formation with a phospholipid, compared with the polycyclic system. The aliphatic chain promotes the solubility of the sterol in the membrane. Decrease in the length of the chain, and the introduction of double bonds into it,

decrease this solubility. At low sterol concentrations (up to 20%), the ordering action of different analogues of cholesterol with shortened chains is practically identical, but increase in the sterol concentration increases this effect only for cholesterol and its closest analogue with an isoheptyl chain, and compounds with a shorter chain at high concentrations no longer dissolve in the bilayer, but form a separate phase.[114,115] At the same time, increase in the length of the side chain to ten carbon atoms alters sharply the properties of the bilayer. This compound, penetrating into the membrane with its long aliphatic "tail", apparently breaks down the neighbouring layer of the bilayer.

Thus the suggestion, put forward as early as 1967,[116] that the sterol in a membrane acts as a "filler" of the space between the hydrocarbon chains of the phospholipid has now been supplemented by a number of requirements which must be satisfied by the sterol structure if it is to be the optimum structure from the viewpoint of the formation of the sterol–phospholipid complex.

In complex formation by sterols with the various groups of chemical substances examined in the present review, a decisive role is played by the planar tetracyclic system. This system, produced in the course of biochemical evolution, is the most favourable for hydrophobic interaction with the aliphatic chains of phospholipids, required for the fulfilment of the normal function of sterols in biological membranes. The two other important structural units of the sterol molecule, namely the 3-hydroxyl group and the iso-octyl chain on C(17), play a lesser role in complex formation. Only complete elimination of the aliphatic chain destroys the ability of the molecule to dissolve in a membrane, but the formation of a hydrogen bond involving the hydroxyl group has not yet been proved. The same polycyclic system interacts even more effectively with the more planar, compared with the chain of the aliphatic acid, rigid alkene system of polyene antibiotics and the planar polycyclic system of saponins. Although the formation of a hydrogen bond with the hydroxyl group of the sterol has not been proved in these cases either, the undoubted requirement of a hydrophilic region in the second component of the complex makes it more probable. Finally, in complexes with simple molecules such as water and acids, the existence of a hydrogen bond has been proved. Here also, however, the hydrogen bond plays a secondary role, orienting the molecules to give the maximum interaction of the gonane rings. The hydrophobic interaction determines complex formation in all the cases examined. This should apparently be taken into account in the study of those sterol complexes about whose structure little is as yet known, in particular lipoproteins.

As already noted, the synthesis of compounds which sorb cholesterol selectively by forming complexes with it is now an important practical problem. Up to the present, success in the preparation of these compounds has been achieved by using derivatives of the natural complex-forming saponins.[10] Synthetic compounds forming complexes of the host–guest type with hydrophobic molecules have proved to be ineffective in the case of cholesterol.[117] These compounds, however, were designed to include as guest molecules small molecules such as benzene, and molecules not containing polar groups.

The material of the present review shows that the possibility of complex formation with sterols is determined by the definite structure of the second component of the complex, in particular its amphipathic nature. This property should apparently be made the basis of the synthesis of compounds capable of forming stable complexes with sterols.

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While the present review was being prepared for publication, several new papers dealing with the formation of hydrogen bonds by sterols appeared. In Refs.118 and 119 it was shown that this bond in carbon tetrachloride solution is identical to the hydrogen bond formed by other alcohols. Papers by the authors of the model of "hydrogen belts" in membranes give some indirect evidence in support of this model.[120,121] The most important paper[122] described the influence of cholesterol ethers (3β-alkoxycholest-5-enes) on the properties of the membranes. The methyl ether of cholesterol alters the permeability of model membranes to almost the same extent as cholesterol, disproving the suggestion that cholesterol acts as a proton donor in hydrogen bond formation with phospholipids. At the same time, the authors cited showed that the influence of cholesterol derivatives on the properties of membranes is due to the presence of the oxygen-containing substituent in position 3 of the sterol, and is determined by the size of this substituent. It was suggested that oxygen may play a role as hydrogen bond acceptor, and that a bond is formed between the oxygen of the sterol and the carbonyl group of the phospholipid via a water molecule.

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# Quantum-chemical Methods in Catalysis

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The methods and various approximations used in quantum-chemical studies of chemisorption and heterogeneous catalysis have been examined, and the principal directions and aims of these studies characterised. Particular attention has been paid to the concept of local centres in heterogeneous catalysis and its realisation in model quantum-chemical calculations. Various types of active centre on the surface of metals and oxides have been examined, and the questions of their quantum-chemical description discussed. Quantum-chemical calculations of the chemisorption and catalytic properties of the Bronsted and Lewis acidic centres of aluminosilicates and related systems have been reviewed.
The bibliography contains 90 references.

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## I. INTRODUCTION

The theory of chemical catalysis is one of the most difficult fields of chemical science. Many problems of organic, inorganic, and metal-complex chemistry essentially converge here. In the case of heterogeneous catalysis, additional problems arise, since it is necessary to take account of the properties of the solid surface. It is possibly only in the last ten years that the extent of the structural complexity and the lability of the properties of the structure of solids has been fully appreciated. It is not surprising that the detailed experimental study of the mechanisms of heterogeneous catalytic reactions encounter considerable difficulties; the complex structure and variety of the active centres (even within a given system) controlling the reaction, their possible modification during the reaction, the variety of intermediate structures produced in the system, the superposition of different reaction channels, changes in reaction mechanisms, etc. all complicate the overall kinetic scheme and make it difficult to understand catalytic processes at the molecular level, so that their interpretation is usually not unambiguous.

The mechanisms of catalytic reactions are mainly studied by direct kinetic experiments (the study of non-stationary kinetic conditions is of particular interest). At the same time, the use of various physical methods to study catalytic systems is raising high hopes. Here, quantum-chemical calculations have been called upon to provide definite assistance.

The aim of the present review is not to provide a complete and systematic picture of the state of affairs in the application of quantum chemistry in catalysis. It is now impossible to do this in a single article, because of the large volume of published calculations. It is necessary to point out, however, that quantum-chemical calculations on individual systems are still fragmentary in character; different authors sometimes reach different conclusions, depending on the models of the active centres and the quantum-chemical methods used.

This feature is still a serious obstacle to the complete systematisation of the results of published studies. Subsequently, therefore, the present review will be restricted to a brief general characterisation of the principal aims and the methods used, and more attention will be paid to the concept of active centres. The review will make practically no reference to such important problems as the calculation of surface states and the rearrangement of the structure of the surface, chemisorption on elemental semiconductors, and lateral interactions of adsorbed molecules. The problems of calculations on chemisorption and reactions on metals will be dealt with to only a limited extent.

It should be emphasised that in the general theory of catalysis, in addition to quantum-chemical methods, whose role is extremely limited, use is made of the methods of statistics and thermodynamics, and physical and chemical kinetics. In addition, formal structural description, etc. is of considerable importance.

It is possible to distinguish three aspects of the application of the methods of quantum chemistry to catalytic systems. Firstly, quantum chemistry provides the most systematic language for describing the structure of catalytic systems and the processes taking place in them, at the electronic level. It is hardly possible at the present time to discuss the individual stages of a catalytic process without the concepts of reactions in $\sigma$- and $\pi$-electronic systems, covalent, ionic, and donor–acceptor bond types, etc. All this provides a basis for understanding the nature of the interactions in catalytic systems at a qualitative level of rigour, and this role of quantum chemistry cannot be underestimated, although it is often masked by specific applications. The possibilities provided by quantum chemistry in this area have not yet been exhausted.

It is possible to take as an example several approaches which in a number of cases may be useful and make it possible to reach simple qualitative conclusions comparatively easily. One of these can be described as the "modified" molecule method. In this case, the changes in the electronic structure of a molecule (the changes in the charges, the energies of individual bonds, etc.) brought about by contact with the catalyst are analysed. This method is used fairly widely in many studies, for example in a series of studies of acid–base reactions on oxides, carried out by the authors of the present review.[1-5]

This approach was developed further in studies[6,7] aimed at analysing the change in the vibronic interactions in molecules when they are coordinated to a catalyst. This approach gives a picture of the intramolecular forces acting on individual atoms and produced on coordination, so that it gives information on the possible deformations of the molecule and the tendency for changes to take place in various chemical properties. In studies of this type, the role of the catalyst reduces either to the transfer of an electron to the molecule or to the capture of an electron from the molecule; alternatively, a model functional group of the catalyst, for example $H^+$, $OH^-$, etc., is taken into account in explicit form in the calculation. In those cases where the influence of the adsorbent on the adsorbate is mainly electrostatic in character (for example a strongly heteropolar support or an individual charged centre), this influence can be estimated using simple electrostatic models.[8] For cubic ionic crystals it is possible to obtain explicit expressions for the electrostatic potential on a regular surface,[9] and in the more general case it is possible to use a system of point Coulombic charges.[10]

Another method of describing the influence of a catalyst on chemical transformations is based on the concept of boundary molecular orbitals. In this case, perturbation theory is usually employed. The application of this method to catalytic problems was developed in Refs.11 and 12.

Metal-complex systems have an important place in both homogeneous and heterogeneous catalysis. Thus in the qualitative quantum-chemical theory of catalysis, particular attention is paid to the analysis of coordinate bonding[13] and to a deeper understanding of the nature of such chemical bonds as the metal–carbene (or carbyne) bond, or M...H–C interactions, which are of considerable importance in catalysis. Here, various aspects of the coordinate bonding of hydrogen in metal complexes are acquiring particular importance.[14]

Secondly, specific applications of the methods of quantum chemistry to catalysis are associated primarily with the study of the elementary act of a given stage of the catalytic reaction, including the chemisorption (coordination) stage. The structural problems which arise in this case can be divided into the following three groups.

a) Calculations of the electronic structure of the assumed active centres (AC), which are generally various structural and impurity defects and surface functional groups. These include calculations of the change in the electronic structure of these active centres as a result of the chemical modification of the catalyst surface in various ways.

b) Estimation of the positions at which the chemisorption of atoms and molecules takes place, the geometry and energetics of chemisorption, comparison of the preference for different chemisorption states, and estimation of the magnitude of the energy barriers to transitions between these states. The investigation of the nature of chemisorption (molecular or dissociative, with or without activation), the determination of the degree of covalent and ionic character in chemisorption bonding, and analysis of the modification of these characteristics with change in the degree of coverage of the surface, etc., solution of the problem of the possible formation during chemisorption of structures with the transfer of ions or charged molecular fragments (carbonium ions, carbanions, etc.).

c) Direct analysis of different paths in the reactions of adsorbed molecules on a surface or in the reactions of adsorbed molecules with surface structures. Comparison of the Eley–Rideal and Langmuir–Hinshelwood mechanisms. Examination of the separate and combined mechanisms of a reaction and the study of the dependence of these channels on different forms of the catalysts, and the use of the results of the calculations for the planning of experiments.

Finally, a third important aspect of the application of the methods of quantum chemistry in catalysis is the calculation of the physical characteristics of surface centres. It was noted above that an important role is played by physical methods for studying catalysts, in particular spectroscopic methods: NMR, EPR, infrared, ultraviolet, photoelectron, X-ray electron spectroscopy, etc. The structural information provided by these studies is increased considerably when parallel quantum-chemical calculations are carried out. Extremely varied structural formations, which as yet have no direct analogues among traditional molecular structures, may be produced on a surface. The only approach, therefore, is to use the results of sufficiently correct quantum-chemical calculations.

Quantum-chemical calculations of chemisorption encounter a fundamental methodological difficulty associated with the need to take account of the interaction of a molecule with the unbounded surface of a solid. The initial stage of the development of the theory of chemisorption was characterised by increased attention to the purely solid-state characteristics of the system, and to the analysis of the types, symmetry, and properties of the zone surface states. This gave many important results; in particular, the conditions for the appearance of Tamm and Shockley surface states were determined. In this approach, ordered chemisorption was

regarded as a change in the structure of the surface states, and the adsorption of isolated molecules was regarded as the appearance of point defects on the surface with a tendency for the capture on this defect of an electron (or hole) from the band states of the solid. A detailed critical analysis of this problem has been carried out,[15] and it will not be dealt with further in the present review.

The development of experimental and theoretical studies of chemisorption led to the conclusion that chemisorption should be regarded rather as the formation of chemical surface compounds. In the theory of heterogeneous catalysis, this was reflected in the chemical concept of catalysis.[16] The determination of the local character of the electronic rearrangements taking place on chemisorption also influenced the quantum-chemical theory of chemisorption phenomena. The effort to obtain a correct description of local chemical bonds and the neglect of the effects of long-range order led to the development of the cluster approach, which involves the separation of a finite (usually small) fragment of the surface (cluster). This method makes it possible to use the methods of quantum chemistry directly.

The cluster approximation is very convenient in quantum-chemical calculations of surface structures. It makes it possible, without difficulty, to construct molecular models of all structural and impurity defects on a surface and models of surface functional groups, and to describe the surface of amorphous solids and alloys. The cluster approximation is also attractive in that it concentrates attention on the chemical nature of chemisorption and catalysis. This approach is now used in most studies involving the calculation of chemisorption. Different versions of the cluster approximation, its unsatisfactory features, and methods for improving its efficiency will be examined below. Various questions related to the choice of the "minimum" clusters for modelling active centres in heterogeneous catalysis have been discussed.[17]

## II. QUANTUM-CHEMICAL METHODS

At the present time, practically the entire range of methods of quantum chemistry, from the simplest semi-empirical methods to fairly complete versions of the non-empirical approach, are used in quantum-chemical studies of chemisorption and surface structures. This situation appears justified, and should be preserved for a fairly long time. This is related, firstly, to the characteristic features of the systems studied: the cluster structures modelling the real surface are extremely extended molecular structures. Moreover, cluster modelling is always indeterminate. It is therefore usually appropriate to analyse a number of versions and to estimate the stability of the results of the calculations when the cluster is expanded; this makes it necessary to carry out a large number of individual calculations. All this requires the use of semi-empirical methods which are as economical as possible.

At the same time, situations often arise in which it is necessary to reach a sufficiently reliable conclusion. Such a situation arises, for example, in the analysis of the possibility of dissociative adsorption or when resolving the question of the reality of certain chemisorption structures. Although experimental methods are constantly improving, it is nevertheless the case that in such a complex and labile system as a surface, the investigation of a number of structural problems still cannot be carried out by experimental methods, and it is here that sufficiently reliable quantum-chemical calculations, carried out using non-empirical methods, may be useful. Moreover, the results of non-empirical calculations for small molecular systems can be used to select and improve the parametrisation of semi-empirical methods. This approach is finding increasing application in problems related to a surface.

Calculation schemes in quantum chemistry are traditionally based either on the method of molecular orbitals (MO) or on the valence bond method.[18] A molecular orbital $\phi_i$ is defined as a one-electron wavefunction describing the movement of an electron in the effective electric field of the nuclei and the other electrons. Usually, $\phi_i$ are represented as a linear combination (LCAO) of atomic orbitals (AO) $\chi_k$

$$\varphi_i = \sum_k c_{ik}\chi_k \,, \qquad (1)$$

The many-electron wavefunction $\Psi$ of a molecular system is expressed as the antisymmetrised product of the spin orbitals, and for closed levels it is conveniently represented as a Slater determinant. This approach is called the restricted Hartree–Fock (RHF) method. The analogous approach, in which the condition that the spatial parts of the spin orbitals $\phi_i^{\alpha}$ and $\phi_i^{\beta}$ for electrons with spin $\alpha$ and $\beta$ be equal is not imposed, is called the unrestricted Hartree–Fock method, and is often used in calculations for systems with open levels (free radicals, triplet and other states, etc.).

A fundamental shortcoming of the Hartree–Fock method is that it neglects the Coulombic correlation of the movement of the electrons. The calculation can be refined by the method of configuration interaction (CI), in which the complete wavefunction $\Phi$ is represented as the superposition of the Slater determinants $\Psi$ for different configurations. With a sufficiently broad basis set in the expansion of Eqn.(1) and allowance for a large number of configurations, it is possible to carry out calculations with a high accuracy, and the accuracy of present-day calculations for small molecules already competes with that of experimental studies.

It is not the purpose of the present review to give details of quantum-chemical calculation schemes; see for example Ref.19. The treatment will therefore be restricted to a formal systematisation with particular attention to those methods which are fairly widely used in calculations on chemisorption and catalysis.

The group of simple semi-empirical MO LCAO methods includes the extended Hückel method (EHM),[20] and its modified form[21] in which additional allowance is made for core repulsion. In Ref.21, an attempt was made to obtain more justified values for the total energy, compared with the ordinary EHM method, in order to optimise the geometry of the molecular systems. This approach (the ASED method) was specially developed for problems of chemisorption and surface reactions, and has been used successfully in a whole series of subsequent studies (calculations of chemisorption and catalysis on metals). The application of the above form of the EHM to oxide systems, which have fairly high ionic character, is formally less justified, however.

The nex group of semi-empirical MO LCAO methods consists of the methods of so-called zero differential overlap. Here it is possible to distinguish two sub-groups, provisionally described as physical and chemical. The first consists of the CNDO/2 and INDO methods, and some of their modified forms.[19] These methods are oriented towards the calculation of electronic characteristics: charge distribution, dipole moments, polarisabilities, spin density, electronic spectra, etc.; that is mainly physical properties. The characteristic features of the parametrisation scheme in these methods make it possible, without particular difficulty, to extend it to the compounds of heavy elements, including 3*d*, 4*d*, and 5*d* transition elements (see for example Ref.22).

The second sub-group consists of the CNDO/BW and MINDO/3 methods, which are oriented towards the calculation of the total energy, heats of atomisation, barriers to conformational transformations, and the geometry of molecular systems. It is these characteristics that are particularly important and interesting in problems of chemisorption and catalysis, but the development of the parametrisation in this case involves much greater difficulties than in the first case. A parametrisation has now been described for the compounds of the elements of the second period (as far as fluorine). A simplified procedure has been proposed[23] for estimating the parameters in the CNDO/BW method, based on correlations with the parameters of the CNDO/2 method.

A parametrisation of the CNDO/BW method has been developed within the framework of the general scheme[24] for calculations on the chemisorption of compounds containing H, C, N, and O atoms on aluminosilicates. The CNDO/BW method gives good results in the calculation of chemisorption on oxides, mainly because this method provides a satisfactory description of hydrogen bonds. One significant shortcoming of the CNDO/BW method, however, is the unsatisfactory description of conjugated organic compounds, which makes it necessary to introduce special corrections. This shortcoming, generally speaking, is not shown by the MINDO/3 method, but the application of this method in chemisorption calculations requires expansion of the parametrisation to the elements of the third and subsequent periods. This problem has been solved for the Si and Al atoms in chemisorption on aluminosilicates.[25]

The problem of expanding the parametrisation of the MINDO/3 method to the 3*d* transition elements is now being studied by several research groups. Thus parameters have been proposed for calculating the chemisorption of hydrogen on iron[26] and on nickel.[27] The MINDO/3 method, however, provides an insufficiently good description of donor–acceptor bonds, particularly hydrogen bonds. In view of the above limitations of the CNDO/BW and MINDO/3 methods, it is appropriate, to control the reliability of the results, by carrying out parallel calculations by these methods.[25] Here, various control calculations carried out by non-empirical methods, and also by MNDO methods, may be of considerable assistance.

The next group of methods consists of calculation schemes in which use is made of a local approximation of the exchange potential: the $X_\alpha$–SW and $X_\alpha$–DV methods.[19] According to the formal classification, these methods occupy a unique intermediate position between semi-empirical and non-empirical methods. The $X_\alpha$–SW method has proved to be extremely effective in calculations of ionisation potentials and electronic spectra, and it is now widely used for these purposes in the cluster analysis of the photoelectron and X-ray electron spectra of chemisorption structures. Certain characteristics of this method make it unsuitable, for example, for calculating the total energy and geometry of these structures. These same characteristic features, however, bring it closer to the methods used in most zone calculations in crystals. The $X_\alpha$–DV method also gives fairly reliable results in the calculation of electronic spectra (although it is less economical than the $X_\alpha$–SW method). The chief advantage of the $X_\alpha$–DV method is that it is possible to carry out fairly good calculations of the energies and the geometry. Very powerful computers are required, however, to realise these possibilities. Nevertheless, the $X_\alpha$–DV method is beginning to be more widely used in the calculation of surface structures and chemisorption.

Non-empirical (*ab initio*) methods form the apex of this quantum-chemical pyramid. Since with catalysis the main interest is in adsorbents containing many-electron atoms (for example transition metals and their oxides), it is appropriate, for the effective utilisation of non-empirical quantum-chemical calculations, to develop the pseudo-potential approximation for the electrons of the core. Most non-empirical calculations of chemisorption on metals are now carried out using this approach. The results of the first calculations using a pseudo-potential for aluminosilicates have now been published.[28] Another important task in non-empirical calculations is to take account of the correlation of the movement of the electrons. In addition to the traditional CI scheme, mention may be made of methods in which partial allowance is made for electron correlation. Among these methods, the generalised valence bond (GVB) scheme,[29] which is oriented towards the solution of problems related to surfaces and chemisorption, has found comparatively wide application in chemisorption calculations.

## III. THE CLUSTER APPROXIMATION

The chief disadvantage of the cluster approach is the rupture of the chemical bonds between the bopndary atoms of the cluster and the rest of the lattice. This results in the production of artificial "surface states", situated partly in the band gap; distortion of the charge distribution; etc. Too many "surface" atome are obtained in the cluster. Unfortunately, to obtain a more correct surface/volume ratio, it is necessary to examine such large clusters that the approach loses its significance. The calculated characteristics of the electronic structure, in which the collective properties of the solid are important, converge slowly with increase in the size of the clusters. This applies to the energy of the Fermi level, the ionisation potentials, the electron affinity, and the atomisation energy.

The cluster approach is completely satisfactory, however, in the calculation of chemisorption, where a decisive role is played by local interactions. Thus even in the case of metals, which is particularly difficult for the cluster approach and where a band gap appears in the cluster calculation, chemisorption calculations for comparatively small clusters give good results. The preferred positions for the chemisorption of molecules, and the geometry, energy, and frequency characteristics of the chemisorption structures, are predicted fairly satisfactorily. Thus for example, in comparative calculations of the chemisorption of atomic hydrogen on Be, going from the $Be_{22}$ cluster to $Be_{36}$, the changes in the equilibrium Be–H distance and the frequency of the stretching vibration of this bond are 4%, and the change in the energy of chemisorption ~20%. The relative stability of the chemisorption states is estimated correctly even for the $Be_{13}$ cluster.[30]

To improve the results of the calculations, in addition to the obvious recommendation that the cluster be expanded, allowance for the influence of its environment, that is the rest of the lattice of the solid, can be proposed. A large number of recommendations of this kind have now been proposed and tested in the literature. This topic has also been reviewed.[31–33] The resulting hierarchy of versions of the cluster approximation makes it possible in principle to construct a bridge to band calculations.[32] At the same time, in the literature, particularly that dealing with chemical problems, use is generally made of simple model methods for taking account of the environment of the cluster; only these will be examined subsequently.

One of the first methods for taking account of the environment of a cluster was based on the introduction of boundary atoms, which were used to saturate the broken outer valence bonds of the cluster ("pendent valencies"). This method

was first used to calculate point defects in homoatomic crystals of diamond and silicon, and H atoms were used as the saturating atoms. The same approach was used successfully to calculate the chemisorption of atomic hydrogen on a graphite surface.[34] In Ref.23, an approach was developed in which the boundary valencies were saturated using univalent atoms whose quantum-chemical parameters (the form of the AO, electronegativity, etc.) were selected to give the best reproduction of various characteristics of the electronic structure of the solid (the stoichiometric charge distribution, the widths of the band gap and the valence band, the orbital composition of the top of the valence band and the bottom of the conductivity band, and various experimentally determined properties of the surface groups). These atoms bounding the cluster were called pseudo-atoms. Corresponding calculation schemes have been developed within the framework of the CNDO/BW[23] and MINDO/3[25] methods, and also the non-empirical method.[28]

This calculation scheme was first used[23] to describe the surface hydroxide groups of silica gel. The parameters of the pseudo-atoms A were selected to give the stoichiometric distribution of charge in a cluster imitating the "volume" of $Si(OA)_4$. The logical consistency of the scheme was verified by analysing the stability of the calculated electronic characteristics (charge distribution, position of the one-electron levels) with respect to expansion of the cluster, that is with successive replacement of the pseudo-atoms A in $Si(OA)_3$.[35] The results of the calculation of the infrared spectroscopic characteristics of the stretching vibrations of the OH bond in the cluster $(HO)Si(OA)_3$ show good agreement with experimental data in the range of both the fundamental $\nu_{OH}$ vibrational band and the overtones, and describe familiar trends in the properties of the OH groups of oxides, namely the comparatively weak dependence of $\nu_{OH}$ on the acidity of the surface OH group, and the marked increase in this dependence when basic molecules are adsorbed.[36]

Different versions of the scheme with boundary pseudo-atoms can be realised. Thus the orbitally stoichiometric cluster method[37] uses a boundary atom with one 3*s* or 3*p* or $sp^3$ orbital of the silicon atom with the AO oriented along the direction of the chemical bond.

Certain difficulties arise when attempts are made to extend the above scheme involving the introduction of boundary atoms into the cluster (which can be called the covalent cluster scheme) to lattices with high coordination numbers ($Al_2O_3$, MgO, ZnO, transition metal oxides). In this case it is more convenient to distinguish an ionic cluster, corrresponding to the ionic model of the lattice. In essence, excess (relative to the neutral cluster) electrons (or an electron deficit) are used to compensate the "pendent valencies", although in this case this terminology is of course fairly arbitrary. The resulting excess of electronic charge can be compensated, to obtain an overall neutral cluster, by an appropriate choice of the charge on the core of the boundary ions.[38]

For the discussion of these two methods of selecting the clusters (covalent and ionic), it is of interest to compare the results of calculations for a given system. This comparison has been carried out for the hydroxide group on an $SiO_2$ surface,[39] the magnetic resonance parameters of paramagnetic surface structures,[40] and a number of models of chemisorption.[41] In spite of certain differences, the two schemes on the whole give similar results. For more definite conclusions, it is necessary to carry out more extensive comparative studies. For close-packed oxide structures, in a number of cases, stoichiometric clusters (for example $Mg_{2n}O_{2n}$) will apparently be preferable, although in these cases also it is appropriate to take account of the Madelung field from the nearest part of the rest of the lattice.

Another method for selecting the cluster is based on the saturation of the "pendent valencies" within the cluster. This approach is convenient when comparing the chemisorption and catalytic activity of active centres of the same kind in different systems; it has been used successfully to compare the acidic centres in aluminosilicates and aluminium phosphates.[24]

## IV. QUANTUM-CHEMICAL STUDIES OF CHEMISORPTION AND CATALYSIS ON METALS

The very first steps are now being taken in the quantum chemistry of catalysis on metals. This is revealed by the fact that the great majority of calculations deal with problems of chemisorption, and the problems of chemical transformations and catalytic reactions are as yet discussed only in a very few papers. From certain trends in the theoretical literature, however, a definite change towards chemical topics may be expected in the near future.

Various metals have been examined in the cluster approximation in quantum-chemical studies. The largest number of published theoretical studies deal with Li, Be, Al, Ni, Cu, and Pt, and to a lesser extent with Na, Fe, Ti, and Ag. The studies have for the most part dealt with the chemisorption of atoms (H, C, O, and various others), diatomic molecules ($H_2$, $O_2$, CO, $N_2$, NO) and simple organic molecules such as acetylene, ethylene, etc. Chemisorption at different positions on various faces of single crystals has been examined; for example, for the (100) face, atomic adsorption on an atom, on a bond, and in a four-coordinate $C_{4\nu}$ position has been studied.

In a number of cases the question of the possibility of surface atomic adsorption and the estimation of the magnitude of the barrier to the transition from the state of an atom above the surface into the surface state has been discussed. An example is the non-empirical calculation of the adsorption of Li, O, and Na atoms on the (111) face of an Al crystal, which was modelled by a three-layer cluster $Al_{19}$ with the (12, 6, 1) structure; the figures give the numbers of Al atoms in the individual layers.[42] The calculation was carried out using a pseudo-potential for the core electrons, so that each Al atom was modelled by a three-electron system (such an extended cluster could be examined only in this approximation). The calculations for $Al_{19}O$ were carried out for a system with $C_{3\nu}$ symmetry with localisation of the O atom on the *z* symmetry axis perpendicular to the surface face of the cluster. Two local energy minima were found, corresponding to one chemisorption state situated above the surface and another situated under it, with octahedral coordination of oxygen. The two states have similar bond energies. The theoretical estimate of the energy of the transition below the surface for the oxygen atom (~2.4 eV), however, was much greater than the experimental estimate of this quantity (~1 eV). The discrepancy is apparently due to the fact that no allowance was made for electron correlation. In the case of Li and Na atoms, no chemisorption bound states were found below the surface. Another example of studies of this kind is provided by Ref.43, where the $X_\alpha$–DV method was used to calculate the adsorption of S, Se, and Te atoms on Ni clusters modelling the (100), (110), and (111) faces.

In calculations of the adsorption of diatomic (and polyatomic) molecules on metals, the question of the dissociative adsorption and fragmentation of the molecules is of particular interest for catalysis. These topics for the most part have been examined using semi-empirical methods of calculation. An illustration is provided by Ref.44, where the CNDO/2 method was used in cluster calculations of the dissociative

chemisorption of $H_2$ on Ni, and also Ref.45, where the dissociative chemisorption of $O_2$ on Ni was examined by the EHM. In those cases where there is a good pseudo-potential approximation for the core electrons, however, it is also possible to carry out non-empirical calculations of this type. For example, the decomposition of methanol on Ni(100) has been examined,[46] and the calculation was carried out by the GVB method for an $Ni_{20}$ cluster. The results of quantum-chemical calculations have also been used[47] to study the role of the *d*-orbitals of metal atoms in the dissociative adsorption of hydrogen on metal surfaces.

Of the published papers on the theoretical study of the fragmentation of organic molecules on metal surfaces, mention may be made of work[48] in which the original form of the EHM was used to examine the localisation of different hydrocarbon fragments ($CH_n$ and $C-CH_n$, where $n = 1, 2, 3$) on the (111) face of a Pt single crystal. The calculation was carried out in the cluster and band versions; it was concluded that allowance for band effects has no significant influence on the results of the calculations. From a comparison of the energies of different chemisorption states for these fragments, the authors cited[48] arrived at the so-called covalent model of chemisorption bonding, in which the most favourable structures are those with complete saturation of the valence of the hydrocarbon fragments; thus for example for CH, $CH_2$, and $CH_3$, three-, two-, and one-coordinate states with respect to the platinum atoms are produced.

The quantum-chemical study of the electronic structure and chemical properties of adsorbed atoms and other structural defects such as steps and vacancies is of particular interest for the discussion of the catalytic properties of metal surfaces. It is widely held that these structures play a unique role as active centres in catalysis. Thus cluster quantum-chemical calculations have shown that certain characteristic features of the electronic structure of the adsorbent, which favour the reactions, can be related to the presence of adsorbed atoms. Thus in a cluster calculation by the $X_\alpha$–DV method it was found[49] that an adsorbed Fe atom on the Fe(111) surface leads to the appearance of new occupied states of *e* symmetry close to the Fermi level, and this may facilitate the dissociation of the CO molecule; this effect was not detected for the adsorption of a Cu atom on Cu(111).

The increased chemical activity of step defects on a Pt surface has been discussed in work[50] where the $X_\alpha$–SW method was used. The calculation shows clearly that these defect structures are coordinatively unsaturated; in the electronic spectrum, a number of orbital states are identified, which lie close to the top of the valence zone and which are directed "away from the surface". The increased chemisorption and catalytic activity of step defects on a surface can also be related to the appearance of these unsaturated valences.

The production of centres with increased activity on metal surfaces may be related not only to structural defects but also to chemical impurities. The influence on the chemisorption of $O_2$ of atomic oxygen in the surface region of Ni(111) has been examined.[45] It was found that in this case there should be a change in the order of preference of adsorbed states, and the most favourable state is one-point adsorption with perpendicular orientation of the molecule. This example of course indicates only that this influence exists, but it may also appear in catalysis.

A cluster calculation (ASED method) of the dissociative adsorption of CO in Ni(111) has been carried out[51] to determine how the dissociation is influenced by the modification of the surface by electron-donor (K, Na) and electron-acceptor (Cl, S) additives. It is known from experiments that the former activate and the latter inhibit the process. The authors cited examined Ni clusters into which a K or Cl atom was introduced, leading to qualitatively different changes in the energy profile along the reaction path; the effect was significant only when the modifying atom entered the immediate environment of the active centre, that is it is fairly local in character. From the qualitative viewpoint, the presence of, for example, the K atom leads to greater population of the MO of the nickel cluster from which, during the chemisorption of CO, partial transfer of electron density takes place to the antibonding $2\pi^*$ orbital of the CO moelcule, facilitating its dissociation. Thus the calculation predicts the production of a negative charge on the CO molecule and an increase in its bond length in this adsorption.

The role of modifying additives may be played by adsorbed reagents, intermediate complexes, and reaction products. This is probably one way of influencing the composition of a reaction mixture during a catalytic reaction on a surface. This provides extensive possibilities for the application of the methods of quantum chemistry. Thus quantum-chemical calculations can be used to look for chemisorption states with an increased chemical activity; an example is provided by a study[52] where a cluster calculation (GVB method) was used to find a quasi-radical adsorption state of an O atom on an Ni surface.

As noted above, there are only a few published papers on the quantum-chemical examination of surface reactions on metals. A typical example is provided by a study[53] where the ASED method was used to calculate the adsorption of CO and O on Pt(111); the calculation was carried out for $Pt_4$ and $Pt_9$ clusters. The Langmuir–Hinshelwood and Eley–Rideal mechanisms for the reaction $CO + O \rightarrow CO_2$ were compared. It was concluded that the energy characteristics of the two reaction channels are similar; the estimated magnitude of the activation energy for the formation of $CO_2$ from adsorbed CO and O was ~1.6 eV, which is close to the experimental value (~1 eV). The chemisorption of Cl, $Cl_2$, and HCl on Fe(100) and the reaction $HCl + O(s) \rightarrow OH(s) + Cl$, where (s) represents the surface form, has also been discussed;[54] the surface was modelled using $Fe_n$ clusters, where $n = 4-21$.

In conclusion it may be noted that the published results of quantum-chemical calculations, together with the results of experimental studies, are sometimes used for a general analysis of important classes of catalytic reaction. An illustration is provided by the discussion of the catalytic hydrogenation of CO on transition metals.[55]

## V. QUANTUM-CHEMICAL STUDIES OF CHEMISORPTION AND CATALYSIS ON OXIDES

In this section, particular attention will be paid to chemisorption and catalytically active centres on the surface of silica and aluminosilicates. Other oxides will be discussed only briefly. This to some extent reflects the thematic distribution of quantum-chemical studies in this field.[56] A series of studies involving quantum-chemical calculations of adsorption on $SiO_2$ can be considered first. Fig.1 shows different possible forms of the adsorption of an $H_2O$ molecule on $SiO_2$. The relative stability of the two forms of $H_2O$ adsorption on a terminal OH group in silica gel has been debated in the literature. A semi-empirical calculation by the CNDO/BW method using a cluster scheme with boundary pseudo-atoms[23] led to the conclusion that form (I) is preferred, in qualitative agreement with experimental data which show that there is only slight perturbation of the frequency characteristics of the hydroxide group when water is adsorbed. A different result was subsequently obtained by

a non-empirical STO-3G calculation.[57] It should be noted, however, that H atoms were used as boundary atoms in the cluster.

The development of a scheme for including pseudo-atoms in non-empirical calculations[28] made it possible to carry out an improved version of this study. This confirmed the conclusion reached in the semi-empirical calculation. The same conclusion was reached in calculations of the adsorption of $H_2O$ on a terminal hydroxide group in $SiO_2$.[58] In this case, the CNDO/2 method with gradual increase in the size of the clusters was used.

Systematic calculations of the adsorption of $H_2O$ on geminal and vicinal pairs of OH groups in silica gel have been undertaken.[59] The energy of the chemisorption of an $H_2O$ molecule on a hydroxide group in silica was estimated as ~10 kcal mole$^{-1}$. The question arose of whether the adsorption of $H_2O$ on a silicon atom is energetically more favourable (form (IV) in Fig.1). Non-empirical calculations[28,60] do not indicate that chemisorption of $H_2O$ and $NH_3$ at an Si atom is possible (as is sometimes assumed). This chemisorption becomes favourable only when there is appreciable deformation of the geometry of the silicon–oxygen tetrahedron (increase in the length of the Si–O bonds, increase in the O–Si–O valence angle), that is only on highly defect structures or on specially prepared surfaces. This apparently provides the answer to the question, discussed in the literature (in the interpretation of experiments and the results of different quantum-chemical calculations), of the production, stability, and prevalence of this form of coordination bonding of $H_2O$ on silica. The details of this discussion cannot be examined in the present review, but references to this topic can be found in Refs.28 and 60.

The CNDO/BW calculation scheme described above has been used[61] to calculate the chemisorption of $NH_3$ at a hydroxide group in $SiO_2$. In this case the most favourable form of adsorption corresponds to the production of a hydrogen bond between the nitrogen atom of ammonia and the hydrogen atom of the surface hydroxide group. The calculation on the whole shows good agreement with the results of infrared spectroscopic studies of the adsorption of $NH_3$ on silica. The adsorption of the molecules of thiophene and thiophane on silica has been calculated[62] by the CNDO/2 method.

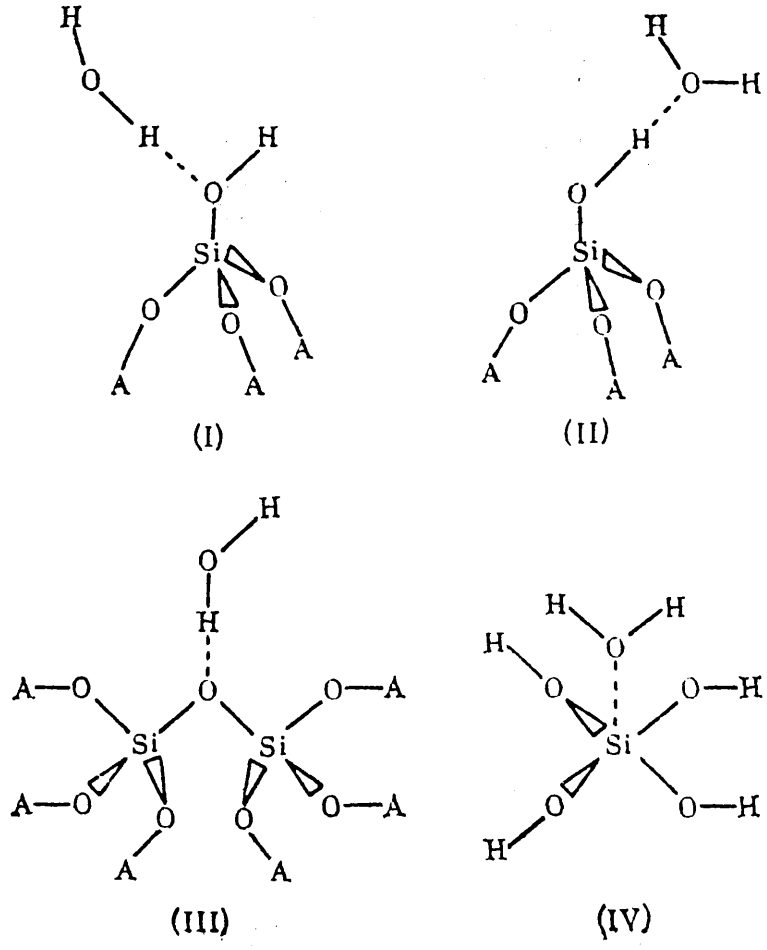



**Figure 1.** Cluster models of the possible forms of adsorption of $H_2O$ on an $SiO_2$ surface; here and subsequently, A represents a univalent pseudo-atom.

Quantum-chemical calculations of the synchronous mechanism of the surface reactions of isotopic H/D exchange between a terminal OH group in $SiO_2$ and molecules of water and hydrogen have been carried out.[23] A systematic study of the influence of change in the acidity of the hydroxide group on the reaction of isotopic H/D exchange with water has been carried out.[63] The most important conclusion from these studies was that the energy barriers of these mechanisms are comparatively low, so that these processes can take place at low temperatures. It was found that the lowest energy corresponds to a transition state with $C_{2v}$ symmetry (compared with $C_{3v}$ symmetry). The extension of this conclusion to other systems indicated, for example, that isotropic exchange between the hydroxide group and an acetylene molecule (where the formation of a $C_{2v}$ transition state is possible) should take place more readily than the corresponding reaction with an ethylene molecule (where only a $C_{3v}$ transition state can exist); this conclusion was subsequently confirmed by direct calculation.[64] The qualitative dependence of these mechanisms on the acidity of the surface group and on the properties of the molecule, obtained in these quantum-chemical calculations, may indicate directions for experimental studies.[63]

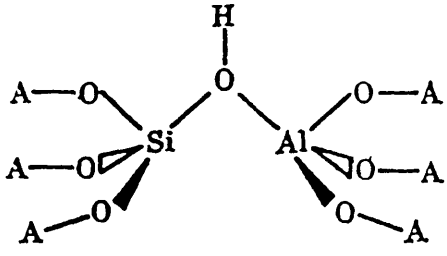



Figure 2. Cluster model of a Bronsted acidic centre in an aluminosilicate.

Quantum-chemical studies of the Bronsted acidic centres (BAC) and Lewis acidic centres (LAC) in aluminosilicates can now be considered. The simplest cluster that can be used to describe a bridging hydroxide group in aluminosilicates is shown in Fig. 2. The results of the calculation show that this group should have much stronger acidic properties than a terminal OH group in $SiO_2$ (estimated from the energy of removal of a proton). In the cluster calculation it was shown that change in the chemical composition of the second sphere (relative to the OH group; for example, by replacing Si by Al + H) leads to an appreciable decrease in the acidity of the OH group; this calculation naturally requires expansion of the cluster shown in Fig. 2. Systematic calculations of this kind, together with allowance for Loewenstein's rule, made it possible to interpret the change in the Bronsted acidity in a series of zeolites with different Si/Al ratios.[65]

Cluster calculations (CNDO/BW method) of the chemisorption of $H_2O$ [59] and $NH_3$ [61] on bridging OH groups in aluminosilicates have been carried out. A non-empirical method has been used[66] to calculate the chemisorption of $H_2O$ on the bridging groups in aluminosilicates. It may be noted that even in the case of the adsorption of the strong base $NH_3$ on an acidic bridging hydroxide group, the calculation does not indicate that the formation of an isolated $NH_4^+$ ion (that is transfer of a proton to $NH_3$) is possible. Preliminary results indicate that this form can be stabilised only by the two-point adsorption of $NH_4^+$ on basic centres of the surface. This indicates the possibility of the easy formation of carbonium ions in these systems, often postulated in the discussion of the mechanisms of acid catalysis. At low degrees of covering, when the effects of solvation in the adsorption layer can be neglected, proton transfer to organic molecules (alcohols, alkenes) should apparently require appreciable expenditure of energy. This in turn raises the question of the possible competition from a synchronous mechanism in these reactions, particularly at lower temperatures.

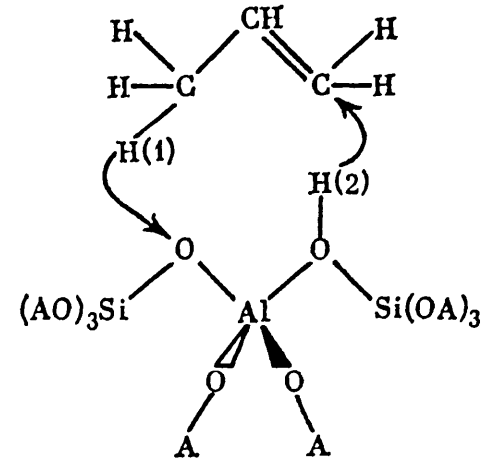



Figure 3. Cluster model of the mechanisms of the isomerisation of propylene on an aluminosilicate surface.

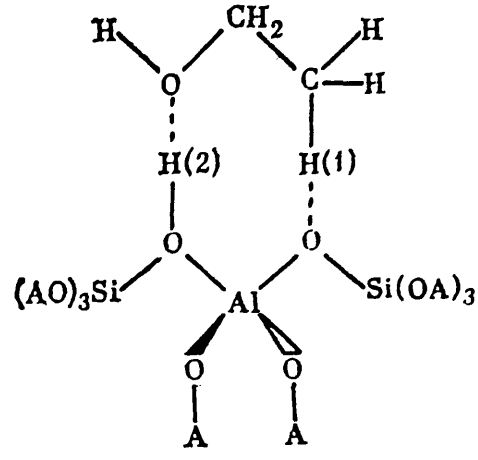



Figure 4. Cluster model of the synchronous mechanism of the dehydration of $C_2H_5OH$ on an aluminosilicate surface.

The carbocation, carbanion, and synchronous mechanisms of the displacement of the double bond in alkenes, catalysed by a birdging hydroxide group in aluminosilicates, have been compared.[67] The cluster examined is shown in Fig. 3; the carbocation mechanism corresponds to the initial displacement of the atom H(2), the carbanion mechanism to the initial

displacement of the atom H(1), and the synchronous mechanism to their simultaneous displacement. The synchronous mechanism of the dehydration of ethanol on the same BAC (Fig.4) has been examined.[68]

As noted above, the most interesting conclusions from these studies are those on the possibility (or difficulty) of the synchronous mechanisms, the factors favouring them (for example the appropriate geometry of the adsorption centre), and the prediction of various qualitative relationships. The latter include, for example, the conclusion that these mechanisms depend comparatively little on the acidity of the hydroxide group; this can be understood qualitatively if account is taken of the fact that the synchronous mechanism involves an acid–base pair, and that a change in acidity in one direction produces changes in the opposite direction in the characteristics of the basic centre, so that there is effective compensation.

The theoretical estimation of the relative specific catalytic activity (within a given system) of different active centres of the same kind, for example BAC, having different structures, is of undoubted interest for catalysis. In addition to a comparison of the strengths of different active centres, this also requires the estimation of their relative concentrations, and definite information on the mechanism of the reaction. The first attempt of this kind at a semi-quantitative level was made[69] in a comparison of BAC of three types in aluminosilicates: a bridging hydroxide group, a water molecule coordinated to an Al atom, and an adsorbed hydroxonium ion. A cluster scheme was used for this calculation. It was concluded that the first two BAC have comparable activities, whereas the concentration of hydroxonium ions is too low. All the studies were carried out for the dehydration of butanols. A quantum-chemical study of different possible BAC in aluminium phosphates, with analogous formulation of the problem,[70] led to the conclusion that the formation of bridging hydroxide groups in these systems is unlikely. In agreement with experiment, the calculation predicts the formation of terminal P–OH groups in these systems. The cluster approach was used to compare the strengths of the BAC in aluminosilicates and aluminium phosphates, and it was concluded that the bridging OH group in aluminosilicates is more acidic than the P–OH group in aluminium phosphates.

A separate series of studies deal with the cluster modelling of the LAC in aluminosilicates.[71–73] It was shown that the exposed three-coordinate Al(1) atom in the pyramidal configuration (see Fig.5) shows all the characteristic properties of an LAC;[72] It has a low-lying unoccupied orbital, localised mainly on Al, and it shows qualitatively the chemisorption properties characteristic of LAC. Estimation of the energies of both molecular and dissociative adsorption on this centre (for $H_2O$, $NH_3$, and $CH_3OH$ molecules), however, gave an unexpectedly high value (several hundred kJ $mole^{-1}$). The calculation was carried out by the CNDO/BW method. Non-empirical estimates led to essentially the same conclusion.

As noted subsequently,[73] however, the chemisorption properties of Al in an oxide lattice may change considerably as a result of the structural coordination of anions. It is possible to have a situation in which only activated adsorption is realised. This last case is illustrated in Fig.5; the localisation of Al in position 2 is energetically more favourable, due to the structural coordination of Al in the lattice. An adsorbed molecule can stabilise the Al atom in position 1, but the change Al(2) → Al(1) generally requires passage over an energy barrier.

It is thus possible to reach the general conclusion that the types of LAC depend markedly on the rigidity of the lattice, and that there is probably extensive dispersion of the properties of the LAC even within a given system; the conclusion that activated adsorption is possible may be the subject of directed experimental studies. A comparison of the strengths of the structural coordination of Al in aluminosilicates and aluminium phosphates[70] indicated that the LAC are stronger in aluminosilicates.

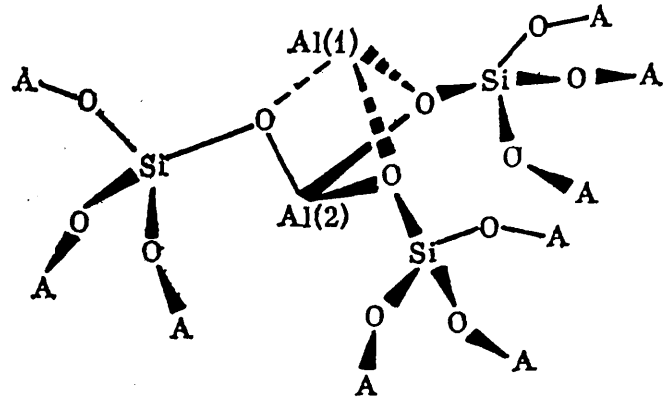



**Figure 5.** Cluster model of a Lewis acidic centre in an aluminosilicate.

The development of the concepts of structural non-rigidity in the systems being considered made it possible to approach in slightly non-traditional fashion the question of the quantum-chemical estimation of the thermal stability of zeolites.[74] Here, the usual approach involves the isolation of the weakest element of the structure. In zeolites, this element is the donor–acceptor bond Al...O. In quantum-chemical calculations, the difference in the strengths of the Si–O and Al–O bonds is revealed, for example, in the difference in the Wiberg indices $P$ of these bonds. By calculating the change in the Wiberg indices $P_{AlO}$ for different forms of zeolite structure, it should be possible to follow the nature of the change in the stability of the zeolite structure. This approach was widely used, for example, in a series of studies[75–78] on the cluster modelling of the structural rings in zeolites, where the influence of the chemical character of the central cation and its effective charge were examined. Although this approach undoubtedly has advantages, it essentially ignores the fact that the stability of a given structure is determined not only by its strength but also by the presence (or absence) of other structural conformations with similar energies.

The examination of the problem of the thermal stability of zeolites by comparing the energies of competing structures opens up new possibilities;[74] in particular, it leads immediately to the conclusion that boralites are less stable than zeolites.

Another type of active centre in zeolites may be cations in cation positions (zeolite windows of different types). These centres have been the subject of an extensive series of studies by Beran and co-workers.[76–78] The calculations were carried out by the CNDO/2 method, and clusters modelling the four- and six-membered "windows" in zeolites and the cations inside them were examined. It is not possible to analyse this entire cycle of studies in the present review; some references to these studies have been given above, and they are examined in more detail in Ref.33.

Finally, brief mention may be made of quantum-chemical calculations on active centres, chemisorption, and reactions in other oxides. As already noted, the cluster modelling of the surface centres of oxide lattices with high coordination numbers encounters certain difficulties. (This feature apparently explains the comparatively small number of calculations of this kind.) An example of this type is the $Al_2O_3$ surface. In this case, quantum-chemical methods have been used to study the properties of the surface hydroxide groups, and also LAC, associated with surface oxygen vacancies. An orbitally stoichiometric cluster, combining Al atoms in octahedral and tetrahedral positions, was used[79-81] to study various surface defects and their chemisorption properties. It was established that the formation of oxygen vacancies leads to the appearance of LAC. The adsorption of $H_2O$, HF, KOH, and $NH_3$ was examined. The calculation showed that fluorination increases the strength of the Lewis activity, whereas the addition of alkali and ammonia weakens it, in agreement with the experimental data. The same approrch was used[81] to examine the dependence of the Lewis acidity on the degree of dehydroxylation of $\gamma$-$Al_2O_3$.

Different defect centres in $Al_2O_3$ have been discussed[82,83] using simple ionic clusters and the EHM and the $X_\alpha$–SW method. Cluster calculations (CNDO/2 method) and a simple qualitative quantum-chemical scheme have been used[24] to carry out a systematic examination of the dependence of the frequency of the $\nu_{OH}$ stretching vibrations of the surface hydroxide groups on $Al_2O_3$ on their immediate environment. The cluster approach (CNDO/2 method) has been used[84] to calculate the chemisorption of ethanol on $\gamma$-$Al_2O_3$; molecular adsorption and two forms of dissociative adsorption were examined.

The possibility of the dissociative adsorption of $H_2$ on an MgO(001) surface has been discussed;[85] the calculations were carried out by a non-empirical method using a minimum ionic cluster. Account was taken of the Madelung field. It was concluded that the dissociation of $H_2$ on a defect-free MgO surface is impossible.

Transition metal oxides form a large and important class of catalysts. Quantum-chemical calculations of the surface centres and reactions on these systems are only beginning. Examples include the examination of clusters modelling the $V^{5+}$ ion in a tetrahedral and octahedral environment of oxygen ions.[86,87] In these studies, the nature of the electron rearrangements taking place on excitation into the singlet and triplet states was analysed. This problem was formulated in relation to various problems in photocatalysis.

An attempt has been made[88] to use the cluster approach to study the reaction of NO with $NH_3$ on a vanadium oxide surface; the CNDO/2 method was used. Different chemisorption structures and a successive series of states along the reaction path were examined; it was concluded that the Eley–Rideal mechanism applies. An unsatisfactory feature of the calculation is that the "pendent valencies" of the cluster were saturated using H atoms, which can hardly be justified for this system. The fact that the results did not change significantly on going to a larger cluster, however, indicates that the qualitative conclusions are correct.

Deposited systems may provide an extensive field of application for quantum-chemical methods, but few studies have as yet been carried out.[89,90]

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To summarise, it can be stated that the application of the methods of quantum chemistry in the theory of surface phenomena and catalysis has now developed into a separate branch of science with its own methodology, experience, success, and failure. This field is now being very actively developed. It is faced with severe methodological problems, associated with the need to improve the calculation schemes (in particular the cluster approximation) and to increase the efficiency of the programs (primarily for non-empirical calculations and calculationd by the $X_\alpha$–DV method). Considerable effort is also required to determine the optimum directions for these studies in catalysis. The latter to a large extent depends on progress in the experimental study of the mechanisms of catalytic reactions, and should be carried out in close contact with experiment.

An increase in the mutual influence of quantum-chemical and kinetic studies can be expected. The greatest problems and the greatest progress in the application of quantum-chemical methods in the study of chemisorption and catalysis are undoubtedly still in the future.

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# Physical Methods for the Investigation of Catalysis *in situ*

O.V.Krylov and A.D.Berman

The principal problems and certain examples of the application of physical methods for investigations in the course of catalysis are examined. The methods for the investigation of the role of phase transformations in heterogeneous catalysis and the application of infrared spectroscopy to the study of surface compounds are considered in greatest detail.
The bibliography includes 65 references.

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## I. INTRODUCTION

The state of both the active catalyst surface and of the structure of its bulk phase differs under the conditions of catalysis from the corresponding state before and after catalysis. The chemical and phase compositions of the catalyst can change during catalysis. The study of the structure of the surface layer and of the bulk-phase and surface phase transformations of the catalyst is essential for the understanding of the nature of selectivity in complex catalytic processes and for the elucidation of the causes of the non-stationary phenomena in heterogeneous catalysis. Hence the necessity for the application of physical (spectroscopic, structural, etc.) methods to direct investigations during the course of the catalytic reaction is evident.

It is possible to distinguish two main problems for the solution of which one employs physical methods in investigations *in situ*, i.e. directly under the conditions of the catalytic process.

1. The elucidation of the structure of the active centre and of the phase composition of the catalyst and also of the changes undergone by them during catalysis.

2. The elucidation of the structure of the surface compounds formed by the reactants and of their role in the catalytic reaction.

X-Ray diffraction analysis, Mössbauer spectroscopy, EPR and other methods are used for the solution of the first problem, while the second problem is solved most successfully by infrared spectroscopy.

In terms of the specific features of their application, the physical methods can be divided into stationary and non-stationary. In the former measurements are performed at a constant temperature and constant reactant concentrations under conditions where there are no changes whatever in the measured quantities as a function of time. In this case the decisive factor is the sensitivity of the method and (a less fundamental factor) the duration of the measurement. For this reason, a method such as, for example, Mössbauer spectroscopy, which requires a long time for the measurement of the spectrum is employed mainly under stationary conditions. The stationary methods make it possible to characterise the chemical or phase composition of the catalyst and the state of its surface in the course of the catalytic reaction. In principle, it is possible to identify also the surface compounds formed under stationary conditions.

By studying the dependence of the rate of the catalytic reaction on the concentrations of the surface compounds measured by physical methods under stationary conditions, it is possible to formulate certain hypotheses about the process mechanism. However, the stationary methods do not permit direct measurements of the rates of the processes occurring on the surface or in the bulk phase of the catalyst, without which it is frequently difficult to assess also their role in heterogeneous catalysis (for example, the involvement of the surface compounds in the reaction). The test of hypotheses about the mechanisms of catalytic processes frequently requires measurements or comparison of the rates of individual stages.

Non-stationary methods are used to solve problems of this kind†. In this case measurements are made of the rate of the catalytic reaction and of the concentrations of various structures in the bulk phase and on the surface of the catalyst under the non-steady-state conditions arising when several parameters are altered: reactant concentrations, temperature, etc. Together with sensitivity, the speed of the response of the apparatus is important in non-stationary measurements. The shorter the time constant of the apparatus the faster the stages susceptible to measurement and the greater the amount of information which can be derived, in principle, about the mechanism of heterogeneous catalysis. We shall consider certain examples of the application of physical methods in the course of catalysis.

This review covers studies where physical methods have been used to investigate the phase transformations of the catalyst and also the surface compounds formed directly under the conditions of the catalysis. The methods most widely used for such purposes are considered: X-ray diffraction analysis, Mössbauer spectroscopy, electron paramagnetic resonance, and infrared spectroscopy. The examples are selected in order to demonstrate specific features and the scope of the application of the physical methods *in situ* and also to reflect the most interesting, in our view, results obtained recently by these methods. More detailed information about the application of physical methods in catalysis can be found in other reviews, references to which are given in the text below.

## II. THE STUDY OF PHASE TRANSFORMATIONS IN HETEROGENEOUS SYSTEMS

### 1. X-Ray Diffraction Analysis

Studies of the changes in the phase composition of the catalyst under the conditions of catalysis present considerable difficulties. The standard high-temperature X-ray cameras are relatively unsuitable for this purpose. With

†The non-stationary methods are also referred to as response or transient methods.

such cameras, it is not always possible to heat the gas phase whose composition is to be monitored. Furthermore, the volume of the cameras is usually too great and precludes the rapid determination of the change in the composition of the gaseous medium as the phase composition of the catalyst is altered.

A differential flow reactor with a small volume (1 $cm^3$) has been developed for the study of the changes in the structure of catalysts during the reaction.[1] The X-ray reactor-camera can be charged with 0.5 g of the catalyst. The reactor has a beryllium window which is transparent to X-rays; at the outlet of the reactor-camera a gas chromatograph is mounted for the measurement of the composition of the reaction products. By recording the changes in the intensities of the individual lines in the X-ray spectrum of the catalyst in the reaction medium, it is possible to measure directly the kinetic parameters of the phase transformation under the conditions of the catalysis.

The study of complex catalysts of selective oxidation have shown that their phase composition, determined on rapid cooling to room temperature, differs from that under the conditions of the catalytic process.[1,2] This result, obtained for nickel molybdates, emphasises the need to investigate the phase composition of the catalyst in the course of the reaction.

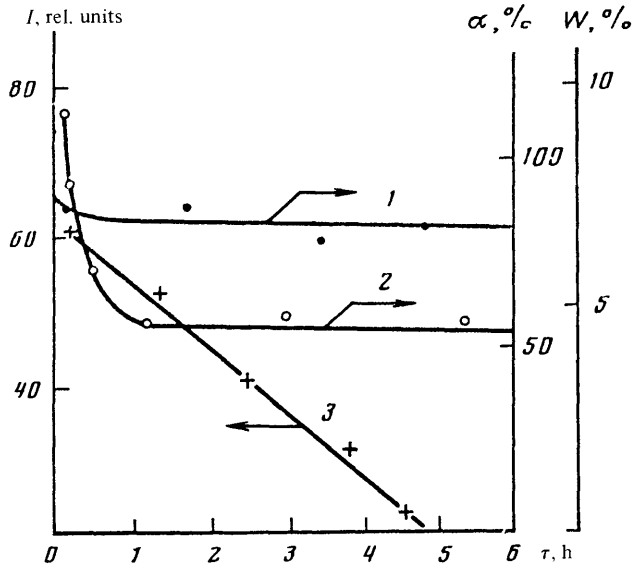



Figure 1. Variation of the degree of conversion α of propene (curve *1*), of the yield of $CO_2$ *W* (curve *2*), and of the intensity *I* of the principal line due to iron(III) molybdate (curve *3*) for the complex Co–Mo–Bi–Fe–O catalyst in the oxidation of propene to acrolein (according to the data of Shiryaev et al.[3]).

The method developed has been used[3] to investigate the phase transformations and rearrangements of the crystal structures of complex oxide catalysts ($Co_6Mo_{12}Bi_{1.0}$, $Fe_{1.5}O_x$, $Mg_6Mo_{12}Bi_{0.75}Fe_{0.35}K_{0.25}O_x$, $Co_6Mo_{12}Bi_{0.75}P_{0.25}O_x$, and $Mo_{12}Bi_{1.0}Fe_{1.5}O_x$) for the oxidation of propene to acrolein. Experiment showed that the iron(III) molybdate present in the complex multicomponent catalysts is reduced during the oxidation of propene at 623 K in a reaction mixture whose composition is stoichiometric for the mild oxidation of propene to acrolein ($C_3H_6:O_2:He = 1:1:8$). It is of interest that no reduction was observed in the experiments with pure $Fe_2(MoO_4)_3$ and mechanical mixtures of $Fe_2(MoO_4)_3$ and $Bi_2(MoO_4)_3$. Fig. 1 illustrates the variation of the contents of different phases in the complex catalyst under the conditions of the catalysis. The content of $Bi_2(MoO_4)_3$ hardly changes. The increase of the intensities of the lines due to cobalt molybdate β-$CoMoO_4$, which is isostructural with β-$FeMoO_4$, accompanied by the simultaneous decrease of the intensities of the $Fe_2(MoO_4)_3$ line indicates the reduction of ferric ions to the bivalent state. The virtually identical parameters of the unit cells of cobalt and iron molybdates lead to the superposition of their lines on the diffractometer traces. Fig. 1 shows that the time taken for the catalytic activity to reach a stationary level is 1–2 h under these conditions. After this, the catalytic activity does not change although the amount of iron molybdate continues to vary. The active centres on the catalyst surface are apparently formed before the rearrangement of the bulk-phase structure of the catalyst is completed.

The phase composition of the deposited $V_2O_5$–$SiO_2$ catalusts has been investigated in the oxidation of tetrahydrofuran (THF).[4] It was shown that the reduction with hydrogen or THF at 200 °C leads to the formation of the $V_4O_9$ phase. After exposure to a mixture of THF and oxygen at 200 °C for 16 h, $V_4O_9$ was also detected together with a small amount of the initial $V_2O_5$ phase.

A phase transition in the orthorhombic molybdenum oxide $MoO_3$ has been observed[5] when a mixture of methanol and helium was passed through the specimen. It was shown that this entails the formation of bronzes having the composition $H_xMoO_3$; dimethyl ether is formed from ethanol. The oxidation of methanol was observed in the $CH_3OH$–$O_2$–He mixture, but the content of the $MoO_3$ phase did not change.

## 2. Mössbauer Spectroscopy

It is possible to distinguish two ways in which Mössbauer spectroscopy can be applied in heterogeneous catalysis: (1) absorption spectroscopy based on the fact that the radiation emitted by a standard radioactive source is absorbed by the "Mössbauer" isotope in the specimen; (2) emission spectroscopy based on the fact that a radioactive isotope, which is in fact used as the source of radiation, is added to the specimen. In this case the radiation is emitted from the specimen itself and is then absorbed by a standard adsorbent containing the "Mössbauer" isotope. We shall examine certain examples of the application of Mössbauer spectroscopy *in situ*.

*(a) Absorption spectroscopy.* Mössbauer spectra were obtained for the first time in the course of a catalytic reaction in a study[6] of the oxidation of propene to acrolein in the presence of complex Co–Mo–Fe catalysts (the composition of the catalysts was indicated above in the description of X-ray diffraction analysis). The Mössbauer spectra were recorded *in situ* in a specially designed small cell (60 ml) which served at the same time as a flow-circulation reactor.[7] The design of the cells for the measurement of Mössbauer spectra *in situ* has also been described.[8,9] Fig. 2, illustrating typical spectra of the Co–Mo–Bi–Fe–O catalysts,[7] shows that under the conditions of the catalysis the singlet line characteristic of the crystalline garnet-like $Fe_2(MoO_4)_3$ is transformed into a four-line spectrum arising from two structurally non-equivalent positions of the iron atoms, Fe(1) and Fe(2), of iron(II) molybdate β-$FeMoO_4$ having the

scheelite structure. However, tervalent iron is also retained in the system, probably in a highly dispersed state, which is not detectable by X-ray methods.

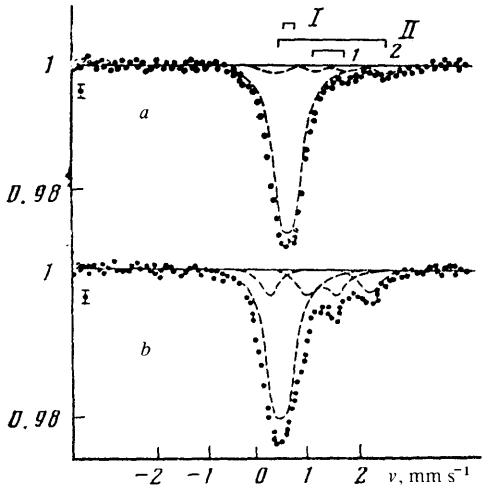



**Figure 2.** The Mössbauer spectra of the Co–Mo–Bi–Fe–O catalyst obtained at 623 K in a stream of $O_2$ (*a*) and in the $C_3H_6 + O_2$ mixture (*b*): I) $Fe_2(MoO_4)_3$ signal; II) β-$FeMoO_4$ signal [1) Fe(1) position; 2) Fe(2) position].

Fig.3 presents the temperature variation of the isomer shift (i.s.) in the Mössbauer spectrum of iron(III) molybdate and of the overall rate of oxidation of propene *w* in the presence of the same catalyst.[7] The continuous line represents the theoretical dependence of the isomer shift on temperature in terms of the classical Debye approximation. The arrows denote the boundary temperatures between the selective and extensive oxidation of propene, which are 680 ± 20 K: the mild oxidation of $C_3H_6$ to acrolein predominates at the lower temperature, while extensive oxidation predominates at the higher temperature. Fig.3 also indicates the values of the relative concentrations *r* of bivalent iron determined from the ratio of the area under the $Fe^{2+}$ spectrum to the overall area of the spectrum.

Fig.3 shows that, in measurements in air (curve *1*), the temperature dependence of the isomer shift is described satisfactorily by the theoretical curve. This can be said also of the experiments *in situ* at 300–520 K. However, at $T \geq 520$ K the isomer shift exhibits a striking anomaly, deviating from theoretical values and reaching a constant value of 0.52 ± 0.02 mm $s^{-1}$ in the region of selective catalysis. In the temperature range 520–680 K the variation of the isomer shift along the dashed curve in Fig.3 is reversible. At 680 K (the onset of extensive oxidation) significant changes take place in the catalyst. The fraction of β-$FeMoO_4$ increases abruptly (*r* rises from 10 to 35%). The temperature variation of the isomer shift is then described by another straight line whose slope differs sharply from the theoretical value. The latter dependence persists in the temperature range 300–750 K both in experiments *in situ* (under the conditions of the catalysis) and in air. The irreversible changes occurring at $T \geq 680$ K in iron(III) molybdate are confirmed also by X-ray data, indicating a change in its structure.

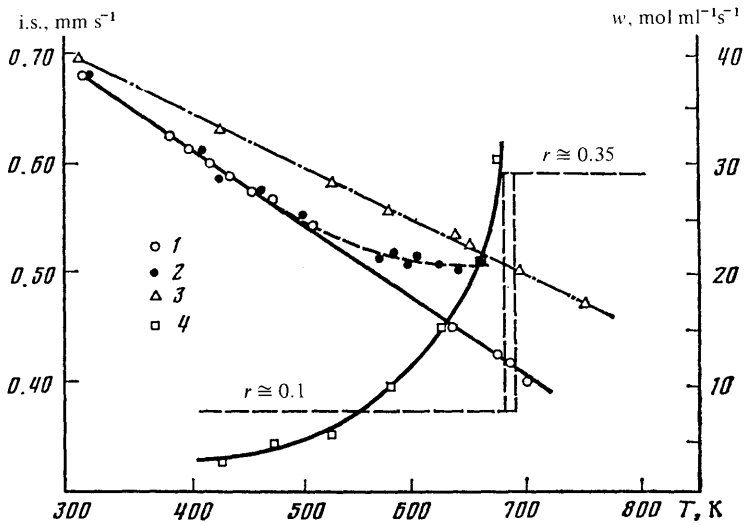



**Figure 3.** Temperature variation of the isomer shifts in the spectra of iron(III) molybdate obtained under static conditions in air (1), *in situ* in the selective oxidation region (2), and *in situ* after experiments at 680 K (3) and the temperature variation of the overall rate of oxidation of propene *w* (4) on the CoMo–Bi–Fe–O catalyst. The dashed band denotes the boundary temperatures between the mild and extensive oxidation processes; *r* = fraction of β-$FeMoO_4$ below and above the boundary temperatures (according to the data of Maksimov et al.[7]).

The results obtained[7] can be accounted for as follows. At the boundary of the iron molybdate crystal anionic vacancies are formed in the course of selective oxidation owing to the removal of oxygen from the $O_L$ lattice in accordance with the following scheme:

$$Fe_2Mo_3O_{12} \rightleftarrows [Fe_2Mo_3O_{12-x}\square_x]^* + xO_L ,$$

where $\square$ is an anionic vacancy. Thermally activated ionisation of the vacancies leads to the appearance of an excess negative charge, which influences the electronic state of the iron ions in the molybdate. In these experiments a change in the spectrum of the entire iron molybdate crystal is observed, indicating a rapid (over a period of $10^{-7}$–$10^{-8}$ s) shift of electron density in the excited $[Fe_2Mo_3O_{12-x}\square_x]^*$ crystal. The iron passes from the $3d^5$ state in the initial crystal to the $3d^{5+\Delta}$ state. The latter is intermediate between the state of iron in the oxidised and reduced iron(III) and iron(II) molybdates respectively.[7] At the iron molybdate–cobalt molybdate interface $Fe_2(MoO_4)_3$ is reduced to $FeMoO_4$, the structural correspondence of $\beta$-$FeMoO_4$ and $\beta$-$CoMoO_4$ promoting the formation of the nuclei of the $\beta$-$FeMoO_4$ phase. A concentration of vacancies $\square_x$ in excess of the equilibrium value is generated at the interface between the iron(II) and iron(III) molybdates in the course of the catalysis. The vacancies, diffusing towards the surface, can serve as centres for the dissociative adsorption of oxygen from the gas phase with formation of $O_L$. Oxygen is apparently absorbed on the $\beta$-$FeMoO_4$ phase. The non-equilibrium polarised $[Fe_2Mo_3O_{12-x}\square_x]^*$ structure constitutes an "arterial highway" supplying the necessary amount of $O_L$ to the active centres for the oxidation of propene to acrolein, which are located, according to the model proposed.[10,11] at the interfaces. In the region of extensive oxidation irreversible changes take place in the $Fe_2(MoO_4)_3$ phases. There is a sharp increase in the amount of $\beta$-$FeMoO_4$, which cannot be fully reoxidised. $C_3H_6$ is oxidised mainly by surface, possibly molecular, oxygen and not $O_L$, with formation of CO and $CO_2$.

The phase transformations in the reduction and reoxidation of the Fe–Mo–O catalyst with the ratio Mo/Fe = 2.4 have been investigated.[12] The reduction of the catalyst with methanol at $T$ < 553 K results in the formation of $\alpha$-$FeMoO_4$. If the specimen is then reoxidised at 600 K, a metastable phase appears, in which $Fe^{3+}$ in a high spin state is located in a distorted octahedron.

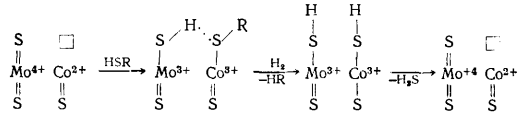
The variation of the composition of the $Fe/Al_2O_3$ catalyst for the Fischer–Tropsch synthesis has been studied.[13] The measurements were made in a steel cell with a beryllium window.[8] The apparatus made possible the mass-spectrometric analysis of the reaction products. It was shown that the rate of reaction in the reduced catalyst reaches a maximum during the first hour of the experiment and then falls. The Mössbauer method has been used to test the hypothesis that the activation of the catalyst is associated with the formation of carbides. Experiment showed that a mixture of the carbides $Fe_{2.5}C$ and $Fe_{2.2}C$ is formed in the presence of CO and $H_2$.

*(b) Emission spectroscpy.* Emission Mössbauer spectroscopy is frequently used to study cobalt-containing catalysts. Such catalysts do not contain an isotope which would permit the employment of the absorption spectroscopy. However, by adding the $^{57}Co$ isotope, it is possible to use it subsequently as a source of radiation in Mössbauer experiments. Information about the cobalt atoms is obtained by studying the signal of the $^{57}Fe$ isotope formed on decomposition of $^{57}Co$. The observed valence and spin states of $^{57}Fe$ can, however, differ from the states of the initial $^{57}Co$ isotope. One of the causes of this difference is that the Co and Fe atoms have different chemical and electronic properties. Furthermore, the decomposition itself can induce unstable but fairly long-lived ($10^{-7}$ s) changes in the environment of the Mössbauer nuclei.[9] A general consideration of the "after-effect" has been described.[14] In conducting materials it can be neglected but the "after-effect" is important in the case of insulators. For example, the $Fe^{2+}$ and $Fe^{3+}$ signals are observed[15] in the emission spectra of CoO, although only $Co^{2+}$ had been detected before decomposition.

However, the "after-effect" is unable to induce a significant displacement of the nuclei, for example, to cause the removal of $^{57}Fe$ from the lattice sites previously occupied by $^{57}Co$. The environment of the $^{57}Fe$ atom is almost identical with that of the $^{57}Co$ atom before decomposition, which makes it possible to employ the emission spectroscopy for the investigation of the catalyst structure. It has been established by this method that cobalt chromite $CoCr_2O_4$ has a direct spinel structure in which the $Co^{2+}$ ions occupy tetrahedral vacancies in the anionic sub-lattice, while the $Cr^{3+}$ ions occupy octahedral vacancies.[16]

In certain cases cobalt-containing phases can be identified by comparing the spectra of the catalysts with those of model compounds. As an example, we shall consider the study of Co–Mo sulphide catalysts for hydrodesulphurisation. It has been shown[9] that in the course of catalysis the Co–Mo–S phase is formed both in the catalysts deposited on the $Al_2O_3$ and in the non-deposited catalysts and has the $MoS_2$ structure. This conclusion is based on the analysis of the spectra of the catalyst obtained *in situ* and on the study of the spectra of a whole series of model compounds ($Co/Al_2O_3$, $CoMoS_4$, $Co_9S_8$, $Co_3S_4$).

A series of $Co–Mo/Al_2O_3$ catalysts with different Co/Mo ratios at a constant molybdenum content have been investigated.[17] The study of the Mössbauer spectra showed that cobalt can enter into three different phases: into the $Al_2O_3$, $Co_9S_8$, and Co–Mo–S lattices. A linear correlation has been obtained between the catalytic activity and the amount of cobalt in the Co–Mo–S phase. According to Topse and co-workers,[9,17] the mechanism of the hydrodesulphurisation is as follows:




Mössbauer spectroscopy is also used in the study of bimetallic catalysts.[18] In cases where one or both metals are active in the Mössbauer effect, it is possible to obtain information about the interactions of the metals with one another or with the carrier. Mössbauer spectroscopy is useful for the elucidation of the positions of the iron ions in the skeletons of zeolite catalysts and their migrations on dehydration of the zeolite. Information about these and other applications of Mössbauer spectroscopy in catalysis can be found in other reviews.[19,20]

### 3. The Method of Electron Paramagnetic Resonance

The EPR method is widely used in catalytic studies because of its sensitivity and the large amount of information which it yields. For example, the method makes it possible to investigate the interaction of oxygen radical-ions with hydrocarbons or the interaction of transition metal ions with the components of oxidation reactions.[21–23]

The difficulties in the employment of the method for the study of catalytic reactions *in situ* at a fairly high pressure, particularly for oxidation reactions, are associated with the broadening of the signal due to the surface ions and radicals after the physical adsorption of $O_2$, $H_2O$, and other molecules on the catalyst surface owing to dipole–dipole interaction. Surface ions or radicals have therefore hardly ever been observed by EPR under the conditions of stationary catalysis.

The EPR method can be used successfully in the study of exchange processes between the surface and bulk of the oxide. Thus it has been shown[24] that the appearance of active centres for the isomerisation of olefins on the $MoO_3$ catalyst is associated with the formation of anionic vacancies on the $MoO_3$ surface and the deactivation of the catalyst is associated with the diffusion of the vacancies into the bulk phase. The diffusion of the vacancies was followed from the EPR signal of the $Mo^{5+}$ ion stabilised in the vicinity of the vacancy.

The EPR method has been used[25] to investigate the phase transformations in $BaTiO_3$, which undergoes a transition from the tetragonal to the cubic phase at 120 °C. This transition could be observed by using impurity $Mn^{2+}$ or $Fe^{3+}$ ions as labels. Owing to local structural distortions in the tetragonal ferroelectric phase, the EPR spectral lines due to $Mn^{2+}$ are broadened, the signal intensity increasing almost by an order of magnitude after the removal of the distortions (on transition to the cubic paraelectric phase). The adsorption of various gases influences the phase transition temperature $T_C$. Only the cubic phase is catalytically active in relation to the oxidation of CO. At low temperatures (130–170 °C) the adsorption and catalytic properties of $BaTiO_3$ are fully determined by the impurity manganese ions. Following the adsorption of CO, the intensity of the EPR signal of the impurity $Mn^{2+}$ ion increases and the amount of $Mn^{2+}$ ions which have appeared is equivalent to the number of CO molecules removed in conformity with the equation:

$$CO + Mn^{4+} + O^{2-}_{surf} \rightarrow CO_2 + Mn^{2+}.$$

On the other hand, $Mn^{2+}$ ions disappear when $O_2$ is adsorbed:

$$2Mn^{2+} + O_2 \rightarrow 2Mn^{4+} + 2O^{2-}_{surf}.$$

A specific feature of the model proposed[25] is that the active centres are present not only on the surface but also in the bulk of barium titanate. The catalytic oxidation of CO takes place via an oxidation-reduction mechanism at a certain constant stationary concentration of $Mn^{2+}$ in $BaTiO_3$, which is determined by the depth of diffusion of the electrons from the $Mn^{2+}$ ions near the surface to the surface. The influence of the phase transition on the catalytic properties of $BaTiO_3$ is associated with the fact that electron transfer from the surface to the bulk phase is possible only in the paraelectric phase.

Another example of phase transformations in the course of the catalysis has been observed in the study of the oxidation of $SO_2$ to $SO_3$ in the presence of vanadium catalysts.[26] The change of the state of the vanadium ions on passing from the melt to the solid state has been followed by EPR. The deactivation of the catalysts and the long relaxation times of the rate of reaction are associated with this process. Studies of the application of EPR *in situ* have also been described in another review.[27]

### 4. Video-LEED—A New Method for the Investigation of Surface Phase Transformations

The methods examined above make it possible to investigate the changes in the bulk-phase structure of the catalyst. A new Video-LEED method (direct observations of the structure from the diffraction of slow electrons) has been developed recently[28,29] and has been used successfully to investigate the rearrangement of the (100) phase of platinum during the adsorption of CO and in the course of the oxidation of CO by oxygen. The method makes it possible to record simulcaneously the intensities of the signals from several two-dimensional structures. At coverages $\theta_{CO} < 0.5$, the $(5 \times 20)$ structure is stable, while at higher coverages the $(1 \times 1)$ structure is stable. The phase transition proceeds via a mechanism involving the formation and growth of nuclei. The transformations of these structures, which take place as the degree of surface coverage is altered, lead to auto-oscillations in the rate of oxidation of CO. A possible relation between the two-dimensional phase transformations and the non-stationary phenomena in heterogeneous catalysis has been indicated.[30] This relation was demonstrated experimentally for the first time by Thiel et al.[28]

We may note that the direct observation of the structure of the surface phase by the Video-LEED method under the conditions of the catalysis is possible only at fairly low pressures ($\sim 10^{-3}$ Pa), where the electrons probing the surface are not scattered by the gas. This applies also to other electronic methods for the study of the properties of the surface (X-ray and photoelectron spectroscopy, Auger spectroscopy, and energy loss spectroscopy with slow electrons), whose application to the study of adsorption and catalysis is still in the initial stage but is developing rapidly.

## III. APPLICATION OF INFRARED SPECTROSCOPY IN KINETIC STUDIES

In order to understand the mechanism of catalysis, it is extremely important to have information about the structure and properties of the surface compounds. It is also important that such data should be obtained directly in the course of the catalysis. Such a possibility is provided, in principle, by infrared spectroscopy. The method yields most information in cases where it is possible to determine quantitatively the concentration of the surface compounds to measure the rate of their formation and consumption, and to compare it with the rate of the catalytic reaction.

In this section we shall consider mainly studies in which infrared spectroscopy was used in kinetic investigations. We shall deal with problems associated with the limitations as regards sensitivity and deviations from the Bouguer–Lambert–Beer law. Other reviews[31–34] have been devoted to other aspects of the application of infrared spectroscopy in catalysis.

In the study of the kinetics of heterogeneous processes, it is essential that the cells used as reactors should make it possible to obtain spectra under the conditions of the catalytic process and should permit a reliable determination of its rate. The present cell designs enable us to carry out catalytic reactions in cells at high temperatures[35] and pressures.[36,37] The flow cells operate under the conditions of a differential reactor for low degrees of conversion. A design for a gradient-free reactor with circulation of the reaction mixture has also been proposed. Since discs containing 20–100 mg of the catalyst are normally used in

infrared spectroscopy, the sensitivity of the detectors usually used for the gas phase may prove inadequate for the detection of the reaction products. In this case an additional amount of the catalyst can be included in the circulation system.[38]

The question of the sensitivity of the method is important. The extinction coefficients in the absorption bands of different functional groups or bonds in a molecule vary within the limits of 2–3 orders of magnitude. Approximate estimates have shown that, under most favourable conditions, concentrations of adsorbed substances of the order of $10^{12}$–$10^{13}$ molecules $cm^{-2}$ can be measured with the aid of conventional spectrometers (without Fourier transformation). In general, one may say that the method is applicable to catalysts with a high specific surface (10–100 $m^2\ g^{-1}$) when conventional spectrometers are employed. Fourier spectrometers, whose sensitivity is higher by two orders of magnitude, make it possible to investigate surface compounds also on industrial catalysts.

## 1. The Bouguer–Lambert–Beer Law

Quantitative measurements by the infrared spectroscopic methods are based on the Bouguer–Lambert–Beer law, from which it follows that the optical density $D$ is proportional to the concentration of the surface compound:

$$D=\varepsilon c l, \qquad (1)$$

where $l$ is the thickness of the disc (cm), $c$ the concentration of the surface compound expressed in terms of the number of molecules per unit volume of the specimen, and $\varepsilon$ the extinction coefficient (molecules$^{-1}$ cm$^2$). The extinction coefficient data for surface compounds are extremely limited; some can be found in Refs. 39–41.

We shall only note that the Bouguer–Lambert–Beer law does not always hold. For example, it is known that interactions between adsorbed molecules can lead to deviations from this law.[42] We shall consider certain experimental data concerning the validity of Eqn. (1) for surface compounds.

Intermolecular interactions are not apparently manifested for low coverages of zeolite catalysts. Thus it has been shown[43] that the Bouguer–Lambert–Beer law holds satisfactorily for formate and acetate complexes formed on interaction of formaldehyde, acetic acid, and acetaldehyde, with NaX zeolite (the concentration of the complexes did not exceed one molecule per cavity). Linear relations have been obtained[39] between the intensity of the absorption band at 1630 $cm^{-1}$ (of the C=C bond) and the concentration of butenes absorbed by NaY zeolite up to the concentrations corresponding to three molecules per large zeolite cavity. However, at high coverages the optical density is almost independent of the amount of butenes absorbed by the zeolite. The Bouguer–Lambert–Beer law holds also for formate complexes on $\gamma$-$Al_2O_3$ [40] at coverages of the order of $10^{13}$ molecules $cm^{-2}$, in the adsorption of CO on platinum deposited on aerosil,[44] and in the adsorption of CO on a number of oxides and zeolites.[45]

At the same time, it has been shown[46] that, for the methoxide ions (absorption band at 2830 $cm^{-1}$) on zinc oxide, the Bouguer–Lambert–Beer law holds only at low optical densities ($D < 0.25$). The interactions in the surface layer can also be manifested by a shift of the corresponding absorption bands as the surface coverage is altered. It has been shown[47,48] that the character of the interaction in the layer following the adsorption of CO on deposited platinum catalysts and in the oxidation of CO on the same catalyst is different. The authors[47,48] attribute this to the formation of "islands" of molecules adsorbed on the catalyst surface in the oxidation of CO. Inspection of literature data has shown that in most cases it is possible to distinguish a linear section on the relation between the optical density and the concentration of certain compounds. However, when quantitative measurements are made, the validity of the Bouguer–Lambert–Beer law must be tested.

We shall now examine certain experimental data obtained in the study of the formation of surface compounds during catalysis.

## 2. Stationary Measurements

Surface compounds have been detected by infrared spectroscopy in a whole series of studies under the conditions of stationary catalysis (see, for example, Bell[37]). However, it is difficult to reach a conclusion about the role of a particular surface compound in catalysis on the basis of stationary measurements, because dead end forms are possible.[37] Under stationary conditions, one can attempt, in principle, to establish correlations between the rate of reaction and the concentration of surface compounds at different reactant concentrations in the gas phase and at different temperatures. Such data might be employed to test kinetic equations. However, hitherto there have been few examples of studies of this kind. In an investigation of the Fischer–Tropsch synthesis on $Ru/Al_2O_3$, $Rh/SiO_2$, $Pt/SiO_2$, and $Pt/TiO_2$ deposited catalysts, no correlations whatever were found between the activity of the catalyst and the concentrations of the surface compounds detected.[49] We may note a study[50] in which it was shown that the rate of hydrogenation of ethylene on the $Pt/Al_2O_3$ catalyst is proportional to the product of the degrees of surface coverage by ethylene ($\theta_e$) and hydrogen ($\theta_H$). It was also found that $\theta_H$ and $\theta_e$ are functions of the ratio of the partial pressures $p_{H_2}/p_e$. In the synthesis of methanol from $CO_2$ and $H_2$ in the presence of catalysts containing CuO, ZnO, and $Al_2O_3$ a clear-cut dependence of the rate on the concentration of the surface formate complexes has been obtained.[51]

One may conclude that the study of the infrared spectra of the surface compounds under stationary conditions is undoubtedly useful. However, in the general case it does not permit a solution of the problem of their role in the catalytic reaction.

## 3. Non-stationary Measurements

Reliable conclusions about the involvement of surface compounds in a catalytic reaction can be reached when data are available for the rates of formation and consumption of these compounds relative to the rate of the catalytic reaction. An effective approach to the problem of identifying the real reaction intermediates involves the study of their dynamic behaviour under the reaction conditions.[52] In this case the experiment consists of the measurement of the concentration of the chemisorbed species under conditions involving sharp changes in the composition of the reactants (for example, when one of them is replaced by its isotopic analogue) and changes in the reaction temperature or the pressure of one of the reactants.

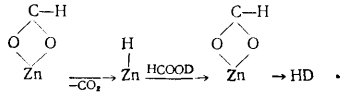
As stated above, a rapid response of the apparatus is important for non-stationary measurements. In the widely used infrared spectrometers without Fourier transform the usual rate of scanning employed to obtain a qualitative

spectrum does not exceed 100 $cm^{-1}$ $min^{-1}$ and the time taken to measure the spectrum in the frequency range 600–4000 $cm^{-1}$ is therefore 30–40 min. When the instrument is tuned to the maximum in a fixed absorption band, it is possible to record processes lasting ~1 s. The rate at which Fourier spectrometers respond can be altered within wide limits—from fractions of a second to several hours depending on the number of scans, which is determined by the required sensitivity of the apparatus. Reports concerning the development of an instrument specially designed for the study of rapid processes have appeared recently; the time taken to traverse half the scale is 0.02 s.[53] A modern apparatus for the study of non-stationary processes by infrared spectroscopy, consisting of an infrared spectrometer, a mass spectrometer and a computer, has been described.[53]

The infrared spectroscopic method is used under non-stationary conditions for the following purposes: (1) for the qualitative test of hypotheses concerning the process mechanisms; (2) for the determination of the kinetic parameters of individual stages occurring with the participation of surface compounds; (3) for a detailed investigation of the kinetics of heterogeneous reactions and for the construction of non-stationary kinetic models.

The decomposition of formic acid on alumina and on silica has been investigated.[52,54,55] It is known that the decomposition of formic acid on various metals and oxides leads to the formation of formate ions and it was assumed that formic acid decomposes via these compounds. However, it was shown with the aid of infrared spectroscopy that the rate of decomposition of formate ions on $Al_2O_3$ is lower by approximately two orders of magnitude than the rate of decomposition of formic acid at the same temperatures and for the same coverages.[52] Experiments were also performed on isotope exchange. After the attainment of the steady state, the formic acid having the composition DCOOD (used as the initial reactant) in the gas phase was rapidly replaced by HCOOH and the variation of the concentrations of the chemisorbed species was followed from the absorption bands at 2915 $cm^{-1}$ ($HCOO^-$) and 2220 $cm^{-1}$ ($DCOO^-$). If the formate ions are intermediates in the decomposition reaction of formic acid, then the $DCOO^-$ ions should be replaced by $HCOO^-$ at a rate equal to that of the catalytic reaction. However, this was not observed experimentally and it was therefore concluded that the decomposition of formic acid does not proceed via formate ions.

In the study of the decomposition of formic acid on zinc oxide at 448–493 K [54] surface formate ions were also detected. Experiments showed that the rate of decomposition is independent of the formic acid pressure and that the ratio of products $CO_2/H_2$ is unity when formic acid is present in the gas phase. On the other hand, when formic acid is removed (frozen out) from the system, the evolution of hydrogen ceases, while the evolution of carbon dioxide proceeds at the previous rate. HD was evolved in the decomposition of HCOOD on zinc formate. It was concluded that the formate ions on the surface of zinc oxide are intermediate species and the following mechanism was proposed for the decomposition of formic acid on ZnO:[55]




Non-stationary measurements have been used[36] to test the hypotheses of the adsorption or impact mechanisms of the oxidation of CO on the $Pt/SiO_2$ deposited catalysts. The surface concentration of CO was deduced from the absorption band at 2074–2080 $cm^{-1}$ (linear form). Fig.4 presents results obtained in experiments where a stream of oxygen was passed through the reactor after the preliminary adsorption of carbon monoxide. The curves describing the time variation of the degree of surface coverage $\theta_{CO}$ show an induction period, which depends on the flow rate. These data suggest that the reaction proceeds via an adsorption mechanism and the presence of the induction period is attributed to the liberation of sites for the dissociative adsorption of oxygen in the course of the desorption of carbon monoxide. The induction period shortens when the temperature is raised as a consequence of the desorption of CO. With increased flow rate, the induction period is also reduced, because the concentration of CO in the gas phase is diminished and the readsorption of carbon monoxide is retarded. Fig.5 presents the results obtained when a stream of CO is passed through the system after the preliminary adsorption of oxygen. Evidently, there is no induction period. The authors[36] explained these results by the establishment of a preadsorption state in the interaction of CO with the platinum surface. Carbon monoxide in this state can react with the adsorbed oxygen (modified impact mechanism) or can pass to a chemisorbed state. Afterwards there is also a possibility of reaction with the adsorbed oxygen (the adsorption mechanism).

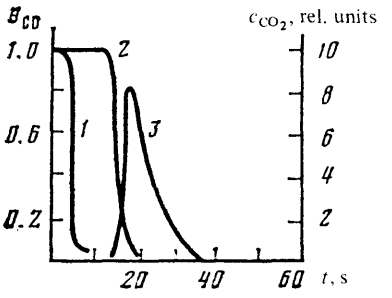



**Figure 4.** Interaction of oxygen with preadsorbed carbon monoxide on the $Pt/SiO_2$ catalyst at 160 °C: 1) and 2) variation of the degrees of surface coverage by CO at flow rates of 133 and 9.5 $cm^3$ $min^{-1}$; 3) variation of the concentration of $CO_2$ in the gas phase (according to Dwyer and Bennet's data[36]).

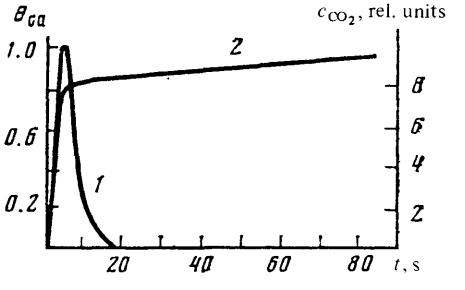



**Figure 5.** The interaction of carbon monoxide with preadsorbed oxygen on $Pt/SiO_2$ catalyst at 160 °C: 1) variation of the $CO_2$ concentration in the gas phase; 2) variation of the surface coverage by carbon monoxide (according to Dwyer and Bennet's data[36]).

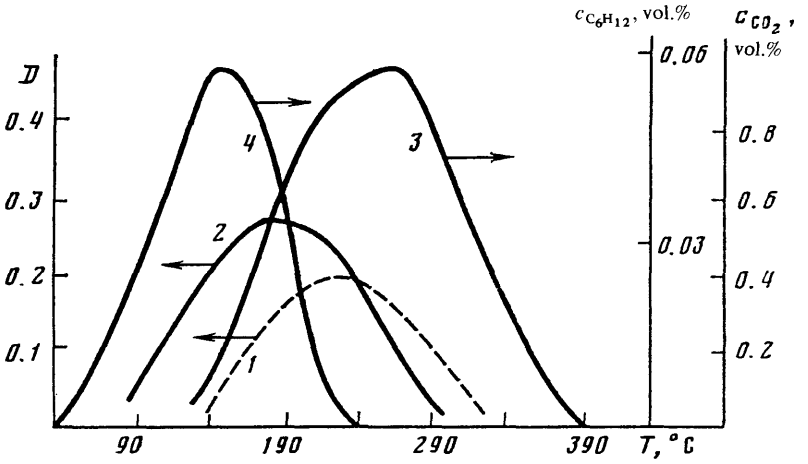



**Figure 6.** The oxidation of cyclohexane on NaX zeolite during programmed heating:[56] 1) and 2) variation of the optical densities in the absorption bands at 1620 and 1710 $cm^{-1}$ respectively; 3) and 4) variation of the $CO_2$ and $C_6H_{12}$ concentrations in the gas phase.

Interesting information can be obtained by combining the infrared spectroscopic and thermal desorption methods. As an example, we shall consider a study[56] of the oxidation of cyclohexane on NaX zeolite. In the course of the extensive oxidation of cyclohexane, carbonyl, formate, and acetate complexes were detected (bands at 1710, 1620, and 1580 $cm^{-1}$ respectively). Fig.6 illustrates the variation of the optical densities of the absorption bands of the surface compounds and the $CO_2$ concentration in the gas phase during programmed heated.[56] Evidently, the carbonyl and carboxylic complexes are formed and decompose at temperatures where $CO_2$ is evolved into the gas phase. These data agree with the hypothesis that the reaction proceeds via the complexes indicated.

The response method combined with infrared spectroscopy makes it possible in many instances to elucidate the mechanism of the reactions of the surface compounds. In particular, an attempt may be made to find the answer to the question whether the surface compounds are formed via a parallel or a consecutive mechanism. For this purpose, the concentrations of the starting materials in the gas phase are reduced sharply (almost to zero) under the conditions of the catalytic reaction. If the concentrations of some surface compounds then increase, while those of others decrease, we have evidence in support of the consecutive mechanism. On the other hand, if the concentrations of the surface compounds do not vary with time, one may use this as an argument in support of the parallel mechanism. It has been shown by this procedure[57] that carbonyl and carboxylate complexes are formed on NaX zeolite from adsorbed cyclohexane via a parallel mechanism. Similarly, it has been possible to demonstrate[58] that the oxidation of propene on the $Bi_2O_3$.MgO and $Bi_2O_3$.$MoO_3$.MgO model oxide catalysts leads to the formation of surface compounds (allyl, polyene, and carboxylate) also via a parallel mechanism.

The question whether the surface compounds detected by infrared spectroscopy are formed on the same or different centres is important for the construction of a kinetic model. If one of these compounds can be obtained on the surface in preliminary experiments, it is then possible to compare the rates of formation of the second compound on the initial catalyst specimen and on the specimen containing the first surface compound. Such data have led to the conclusion that the carbonyl and carboxylate complexes are formed on different centres in the oxidation of cyclohexane on NaX zeolite (Fig.7).[57]

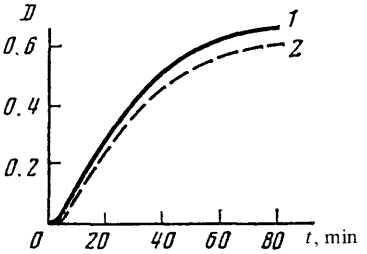



**Figure 7.** Time variation of the optical density in the 1710 $cm^{-1}$ absorption band at 368 K: 1) stream of cyclohexane directed to a conditioned NaX zeolite specimen; 2) stream of cyclohexane directed to the NaX zeolite after the preliminary formation of carboxylate complexes on the latter.[57]

In a whole series of studies the infrared spectroscopic method has been used to determine the rate constants and activation energies for individual stages of heterogeneous reactions. The effective activation energy has been found[59] for the overall process involving the hydrogenation and desorption of surface compounds formed in the hydrocracking of n-hexene on nickel and platinum. The activation energies for the oxidation of the carboxylate complexes formed in the oxidation of propene on $Cr_2O_3$ and NiO have been determined.[60] The results proved close to the activation energies for the oxidation of propene obtained in a gradient-free reactor. On this basis, it was concluded that the carboxylates are intermediates in the oxidation of propene on $Cr_2O_3$ and NiO and that the rate-limiting stage is the oxidation of the carboxylate. We may note that, generally speaking, comparison of the activation energies is insufficient to reach this type of conclusion.

The effective activation energies for the oxidation of the surface forms of CO adsorbed on CoO–MgO solid solutions and MgO have been obtained.[51,62]

The kinetics of the reactions of a series of surface compounds, namely π-allyl (1510 $cm^{-1}$), a polyene (1605 $cm^{-1}$), a carboxylate (1580 and 1430 $cm^{-1}$), and a propene degradation product (1340 $cm^{-1}$), formed in the oxidation of propene on the $Bi_2O_3$.MgO and $Bi_2O_3$.$MoO_3$.MgO model oxide catalysts, have been investigated[58] by infrared spectroscopy in the temperature range 200–400 °C. The introduction of molybdenum ions into the $Bi_2O_3$.MgO catalyst sharply reduces the activation energies for the formation and decomposition of the π-allyl complex.

Despite the comparatively large number of studies in which infrared spectroscopy was used directly in the course of catalysis, there have been almost no investigations in which the kinetics were studied in detail and a kinetic model constructed on the basis of the study of the surface compounds. One of the few examples of this kind involves the investigation of the oxidation of cyclohexane on NaX zeolite.[63,64] The authors of the review[63] studied the kinetics of the oxidation of the oxygen-containing complexes formed in the oxidation of cyclohexane under isothermal conditions and during programmed heating; the results are presented in Table 1. They made it possible to compare the rate of oxidation of the complexes with the rate of the catalytic reaction. The rate of oxidation of the complexes was calculated from the formula

$$w = \epsilon D_{st} k, \qquad (2)$$

where $D_{st}$ is the stationary optical density in the catalytic experiments, $k$ the rate constant for the oxidation of the corresponding complexes, and ε an experimental coefficient.

Table 1. The activation energies $E$ and the pre-exponential factors for the oxidation of the surface complexes.

| Complexes (spectral band) | $E$, kJ $mol^{-1}$ | | $k_0$, $s^{-1}$ | |
|---|---|---|---|---|
| | thermal desorption | isothermal experiments | thermal desorption | isothermal experiments |
| Carbonyl (1710 $cm^{-1}$) | 92 | 92 | $1.1 \cdot 10^7$ | $6.1 \cdot 10^6$ |
| Formate (1620 $cm^{-1}$) | 75 | 75 | $5.3 \cdot 10^4$ | $5.3 \cdot 10^4$ |
| Acetate (1580 $cm^{-1}$) | 63 | 63 | $3.4 \cdot 10^2$ | $2.2 \cdot 10^2$ |

For low degrees of conversion, the flow cell can be regarded as a differential reactor and the rate of extensive oxidation was therefore calculated from the equation

$$W = F c_{CO_2}, \qquad (3)$$

where $F$ is the flow rate and $c_{CO_2}$ the concentration of carbon dioxide in the gas phase.

The results of the comparison of the rates of the catalytic reaction ($w_{CO_2}$) and of the oxidation of the surface compounds—the carbonyls ($w_{1710}$), the formates ($w_{1620}$), and the acetates ($w_{1570}$)—are presented in Table 2. Their comparison shows that the overall rate of oxidation of the surface compounds $w_\Sigma$ is close to the rate of the catalytic reaction. One may conclude that the extensive oxidation of cyclohexane proceeds via the formation and oxidation of the carbonyl and carboxylate complexes and that the carbonyl complexes make the greatest contribution. A kinetic model, all stages of which have been demonstrated directly, has been proposed[64] on the basis of the results. The model reproduces correctly the changes in the concentrations of the surface compounds and the $CO_2$ concentration under non-stationary conditions; the stationary rates of reaction and the concentrations of the surface compounds also agree satisfactorily with the experimental values. The kinetic parameters of all the stages have been determined.

Table 2. Comparison of the rates of the catalytic reaction and of the oxidation of the surface compounds ($cm^3$ $min^{-1}$).

| $T$, K | $w_{1700}$ | $w_{1620}$ | $w_{1570}$ | $w_\Sigma$ | $w_{CO_2}$ |
|---|---|---|---|---|---|
| 493 | 0.07 | 0.02 | 0.007 | 0.09 | 0.13 |
| 513 | 0.13 | 0.03 | 0.08 | 0.17 | 0.13 |
| 533 | 0.22 | 0.04 | 0.01 | 0.27 | 0.27 |
| 568 | 0.32 | 0.06 | 0.013 | 0.4 | 0.34 |

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In conclusion we may note that new vibrational spectroscopic methods are developing rapidly, including the characteristic slow electron loss spectroscopy (EELS), the inelastic electron tunnelling spectroscopy (IETS), and Raman spectroscopy with a laser source (laser-Raman), which is widely used in the study of surface compounds. However, the number of examples involving the use of these types of spectroscopy in studies directly under the conditions of catalysis is as yet small. Studies of catalysis *in situ* by infrared-Fourier spectroscopy have begun to be published recently.[53,65]

The experimental techniques for the investigation of catalysis by spectroscopic methods are developing rapidly. It is to be expected that the role of spectroscopic methods in the investigation of catalysis *in situ* will increase sharply as the sensitivity and rapidity of the response of the apparatus are improved.

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# The Study of Heterogeneous Catalysis by Nuclear Magnetic Resonance

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The use of modern NMR Fourier spectrometers to study heterogeneous catalysts and molecules adsorbed on their surface has been examined. Data obtained in the study of vanadium catalysts for the oxidation of sulphur dioxide; the state of aluminium and silicon in aluminium and silicon oxides and in zeolites; hydroxide groups; and platinum in deposited platinum catalysts, and also the first data on the $^{17}O$ NMR of oxide catalysts, have been summarised. The results of the study of adsorbed molecules, including the use of the high-resolution NMR spectroscopy of solids, have been discussed.
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## I. INTRODUCTION

Nuclear magnetic resonance (NMR) is one of the basic modern physical methods of study in chemistry. The high sensitivity to changes in the structure of molecules and to intermolecular interactions, the possibility of quantitative analysis, and the simplicity and reliability of the interpretation of the spectra have made NMR an important instrument in the study of the structure and reactivity of substances in solution.

In homogeneous catalysis, NMR has for a long time been widely used to establish the structure of catalytically active complexes, and to study ligand exchange, intramolecular rearrangements, inner-sphere and outer-sphere coordination of solvent molecules to molecules of the catalyst, the formation of intermediate complexes between the catalyst and the substrate, etc. (see the earlier review[1] and references therein). In heterogeneous catalysis, however, NMR has until recently been much less frequently used, since the study of solid catalysts and adsorbed molecules by this method is complicated by the much larger (by a factor of approximately $10^3$–$10^4$) NMR line width in the case of solids, compared with liquids. The marked broadening of the lines, firstly, decreases sharply the sensitivity of the method and, secondly, generally leads to a loss of information on the most important characteristics of the NMR spectra, namely the chemical shifts and spin–spin coupling constants. The decrease in sensitivity is particularly marked, since heterogeneous catalysts often consist of elements for which the nuclei of the magnetic isotopes either have low natural concentrations (for example 0.037% for $^{17}O$, 8.6% for $^{119}Sn$, etc.) or have a small magnetic moment ($^{27}Al$, $^{51}V$, $^{63}Cu$, $^{65}Cu$, $^{11}B$, $^{9}Be$, $^{71}Ga$, etc.). On the other hand, the study of adsorbed molecules is often made difficult by the small quantity of the substance being studied in the specimen.

At the same time, in principle, the NMR spectra of solids carry much more information on the structure of a substance than the spectra of liquids. This is related to the fact that many interactions which are averaged in liquids as a result of the thermal motion of the molecules are fully revealed in the spectra of solids; this makes it possible to obtain valuable information on the structure of crystals and the chemical bonding in them. For example, dipole–dipole interaction is not revealed in the spectra of liquids; in the case of solids, it carries information on the relative arrangement of atoms. Analysis of the temperature dependence of the dipole contribution to the line width makes it possible to study nuclear movements of different kinds in solids. Quadrupole interactions are also averaged in liquids, but their study in solids makes it possible to obtain information on the distribution of charges around a nucleus. In the spectra of liquids, the chemical shift is described by a single parameter, namely the isotropic magnetic shielding constant, whereas in the spectra of solids it is characterised by the three components of the magnetic shielding tensor, that is it contains much more information on the chemical bond than can be obtained from the NMR spectra of liquids.

A characteristic feature of NMR spectra is that in solids the interactions of different types often have similar orders of magnitude. Thus to obtain the required information it is necessary to separate from the spectrum the parameters characterising the interactions of a definite type. This makes it necessary to carry out additional experiments involving measurements at different frequencies and over a range of temperatures, the computer calculation of spectra, etc. The development of a new generation of NMR spectrometers which make it possible to carry out measurements in strong magnetic fields (~7 T) with Fourier transformation of the NMR signal, and also the use of different methods for decreasing the line width (the high-resolution NMR spectroscopy of solids), have led to qualitative changes in the possibilities provided by NMR in the study of heterogeneous catalysts and adsorbed molecules.

Most importantly, the use of strong magnetic fields and the rapid accumulation of signals by Fourier transformation, together with the marked increase in the volume of the specimen, has led to a sharp increase in the sensitivity of the method, making it possible to proceed to systematic studies of NMR involving the nuclei of various elements present in catalysts and adsorbed molecules. Fundamentally new possibilities for the study of catalysts appeared as a result of the application of the methods of the high-resolution NMR spectroscopy of solids, such as rotation of the specimens with a high frequency at the magic angle to the external field (MAS, or VMU in Russian) and the use of pulse sequences, which lead to a decrease in the line width in the spectra of solids. The use of these methods makes it possible to average some interactions, leaving others unchanged, and hence to analyse separately interactions of different types. In a number of cases these methods make it possible to obtain spectra with a resolution comparable with that of the spectra of liquids.

This considerable expansion of the possibilities provided by the method has led to the appearance in recent years of a large number of studies of adsorption and heterogeneous catalysis by NMR spectroscopy. The present review examines the principal results of studies in this field carried out in the period 1976–1983. Earlier studies were examined in earlier reviews.[2–4] The possibilities provided at present by NMR spectroscopy in this field are demonstrated, and new data on the structure of a number of important catalysts and on the mechanisms of adsorption and catalysis, obtained by this method, are also discussed.

## II. THE HIGH-RESOLUTION NMR SPECTROSCOPY OF SOLIDS

This rapidly developing branch of NMR spectroscopy[4–10] is extending considerably the possibilities provided by the method in the study of catalysts and adsorbed molecules.

The principles of the methods of high-resolution NMR spectroscopy of solids, most frequently used in the study of catalysts and adsorbed molecules, are described below.

### 1. The Principal Interactions in NMR Spectroscopy

The Hamiltonian $\mathcal{H}$ describing the NMR effect in solids consists of several terms:[11,12]

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_Q + \mathcal{H}_D + \mathcal{H}_\sigma + \mathcal{H}_E + \mathcal{H}_{rf} \qquad (1)$$

Here, $\mathcal{H}_z$ is the Zeeman term characterising the interaction of the magnetic moment of the nucleus with the external magnetic field; $\mathcal{H}_Q$ the Hamiltonian of the quadrupole interaction, significant for nuclei with $I > 1/2$; the spectroscopic parameters determined by this term carry information on the electric field gradient at the point where the nucleus is situated; $\mathcal{H}_D$ the Hamiltonian of the dipole–dipole interaction; the parameters determined by it carry information on the relative positions of the nuclei; $\mathcal{H}_\sigma$ the Hamiltonian of the chemical shift characterising the shielding of the nuclei by electrons; measurement of the parameters determined by this term makes it possible to identify the chemical state of the atom; $\mathcal{H}_E$ the Hamiltonian describing the interaction of the magnetic moments of the nuclei with the magnetic moments of unpaired electrons; it is important for paramagnetic materials; the parameters determined by this term contain information on the relative positions of the nuclei and the unpaired electrons and on the nature of the chemical bond; and $\mathcal{H}_{rf}$ the Hamiltonian of the radiofrequency field used to observe the NMR (and to change the average values of the other terms in Eqn.(1)).

Since the terms of the Hamiltonian (1) depend on the angular coordinates in different ways, they change in different ways under the influence of molecular motion, as a result of rotation of the specimen, or under the influence of radiofrequency pulses. These changes depend on the frequency and anisotropy of the averaging action. The main idea in the high-resolution NMR spectroscopy of solids is to apply to the system of nuclear spins a strong perturbation organised in such a way as to suppress (average) some of the interactions, and hence to make it possible to study other interactions in purer form. If different perturbations are used, it is possible in principle to obtain detailed information on each interaction separately.

Before the methods of high-resolution NMR spectroscopy are described, the principal interactions of importance for the description of the NMR spectra of solids will be examined in slightly more detail; for simplicity, the treatment will be restricted to the case of diamagnetic crystals.

#### *a) Dipole–Dipole interaction*

The Hamiltonian of the direct dipole–dipole interaction in a strong magnetic field between nuclei having magnetic moments has the form:[11]

$$\mathcal{H}_D = \sum_{i<j} \frac{1}{2} \gamma_i \gamma_j \hbar^2 r_{ij}^{-3} (1 - 3\cos^2\theta_{ij}) [\vec{\mu}_i \vec{\mu}_j - 3(\mu_z)_i (\mu_z)_j] \qquad (2)$$

Here, $\gamma_i$ and $\gamma_j$ are the gyromagnetic ratios of the nuclei $i$ and $j$; $r_{ij}$ the distance between the nuclei; $\theta_{ij}$ the angle between the direction of the external magnetic field and the vector joining the nuclei $i$ and $j$; $\vec{\mu}_i$ and $(\mu_z)_i$ the vector of the magnetic moment of the nucleus $i$ and its projection on the direction of the external magnetic field; and $\hbar$ Planck's constant. The Hamiltonian of the dipole–dipole interaction depends markedly on the relative positions of the nuclei, so that the spectroscopic parameters characterising this interaction carry information on the relative positions of the nuclei in the solid. Movement of the nuclei leads to a change in $\mathcal{H}_D$ with time, and may change the NMR spectrum (if the frequency of the motion is sufficiently high). Thus the dipole–dipole interaction is also used to study dynamic processes in solids (diffusion, restricted rotation, etc.).

Studies using direct dipole–dipole interaction to obtain information on the positions of nuclei and on their motion in solids until recently made up the greater part of studies on the NMR spectroscopy of solids. In practice, however, the data obtained can be interpreted quantitatively in terms of interatomic distances usually only for solids with a simple structure or in those cases where the solid contains isolated groups consisting of a small number of nuclei, for which the Hamiltonian has a comparatively simple form. With increase in the number of interacting nuclei, the form of the spectrum becomes much more complicated, and its width increases. As a result of the strong orientational dependence of the Hamiltonian $\mathcal{H}_D$, the broadening of the spectra is particularly marked for polycrystalline specimens; in these cases the NMR spectrum is most frequently characterised by only a single parameter, the second moment of the spectrum. This field of study of usually called low-resolution NMR spectroscopy or broad line NMR spectroscopy.

#### *b) Chemical shielding*

The movement of the electrons surrounding the nucleus produces an additional magnetic field, which, combined with the external magnetic field $H_0$, creates an effective field $H_{\text{eff}}$ at the point where the nucleus is situated.[11] To take account of this fact, the magnetic shielding tensor $\hat{\sigma}$ is introduced into the expression for the Hamiltonian of the chemical shift:

$$\mathcal{H}_\sigma = -\mu(1 - \hat{\sigma}) H_0 \qquad (3)$$

The magnetic shielding tensor is a tensor of second rank; it is often also called the chemical shift tensor. It contains information on the electronic environment of the nucleus and on the chemical bonding in the crystal. The chemical shift tensor is described by six independent parameters—the three principal values of the tensor and the three angles which characterise the positions of the principal axes of the tensor relative to the axes of the crystal. It is possible to obtain all of these quantities only from the NMR spectra of single crystals. The spectra of polycrystalline specimens can give only three parameters—the principal values of the tensor $\hat{\sigma}$.

Systematic measurements of chemical shift tensors for solids became possible only after the development of the methods of high-resolution spectroscopy, since the chemical shifts are usually smaller than the dipole broadening, and therefore do not appear when ordinary methods are used to record the NMR spectra of solid specimens. In liquids, where the rapid molecular motion averages the dipole interactions, there are no obstacles to the measurement of the chemical shifts. The molecular motion averages the chemical shift tensor in such a way that only its average value is measured; even the average value of the tensor, however, is exceptionally informative.

The methods of the NMR spectroscopy of solids make it possible to measure all three principal values of the tensor $\hat{\sigma}$, so that more information is obtained. For example, the deviation of the electron density distribution round the nucleus from spherical symmetry is reflected in the difference between the principal values of $\hat{\sigma}$, whereas the average value of the chemical shift carries only indirect information on this deviation. In addition, measurements of the temperature dependence of the anisotropy of $\hat{\sigma}$ make it possible to detect and study various movements within solids, in particular anisotropic movements.

*c) Quadrupole interaction*

The Hamiltonian of the quadrupole interaction carries information on the electric field gradient $V$ at the point at which the nucleus with $I > 1/2$ is situated:[11]

$$\mathcal{H}_Q = \frac{e^2qQ}{4I(2I-1)}[3\hat{I}_z^2 - \hat{I}^2 + \eta(\hat{I}_x^2 - \hat{I}_y^2)] \qquad (4)$$

Here, $eq = V_{zz}$, $\eta = (V_{xx} - V_{yy})/V_{zz}$, and $eQ$ the quadrupole moment of the nucleus; the $z$ axis is directed along the external magnetic field $I_+ = I_x + iI_y$. The energy of the quadrupole interaction is usually much lower than the energy of the Zeeman interaction, and the influence of the quadrupole interaction on the spectra is revealed in first- and second-order perturbation theory. In first-order perturbation theory, the Zeeman levels are displaced by an amount which depends on the projection of the magnetic moment of the nucleus on the direction of the external field. This leads to the appearance of $2I$ lines in the NMR spectrum. For nuclei with half-integral spins, the central transition ($-1/2 \leftrightarrow 1/2$) remains unchanged in first-order perturbation theory. In second-order perturbation theory, the central transition is split, and its centre of gravity is displaced; the values of the splitting and the shift are inversely proportional to the magnitude of the external magnetic field.

The Hamiltonian of the quadrupole interaction may be so large that the displacements of second order will be close to (or greater than) the values of the chemical shift and the dipole contribution to the line width, particularly for measurements at low frequencies. The main difficulty in the recording of the NMR spectra when there are large quadrupole contributions is due to the marked broadening of the lines as a result of the non-uniformity of the electric field at different points in the specimen, and also as a result of the angular dependence of the energy of the quadrupole interaction (in the case of polycrystalline specimens). In these cases, for nuclei with half-integral spins, information can be obtained from measurements of second-order effects for the central transition.

## 2. Methods for Decreasing the Line Widths in the Spectra of Solids

*a) Rotation of the specimen at the magic angle*

Rapid rotation of the specimen about an axis directed at the so-called "magic" angle of 54°44', to the external magnetic field may lead to a considerable decrease in the line widths in the NMR spectra.[9,13-17] This follows from an examination of the expressions describing the Hamiltonians $\mathcal{H}_D$, $\mathcal{H}_\sigma$, and $\mathcal{H}_Q$ in Eqn.(1).

The Hamiltonian of the dipole–dipole interaction (2) can be considered first. When the specimen is rotated, the angle $\theta_{ij}$ between the external magnetic field and the vector $\vec{r}_{ij}$ depends on time, and the difference $(1 - 3\cos^2\theta_{ij})$ takes both positive and negative values. Analysis of expression (2) shows that rotation of the specimen about an axis coinciding with the direction of the field has no influence on the spectrum; rotation about an axis perpendicular to the field decreases the line width by a factor of 2; and rotation about an axis making an angle of 54°44' with the direction of the field ($\cos^2 54°44' = 1/3$) averages the dipole–dipole interaction to zero. The physical significance of this phenomenon is that when the rotation is sufficiently rapid, so that $h\nu$ (where $\nu$ is the frequency of the rotation, and $h$ is Planck's constant) is greater than the energy of the dipole–dipole interaction, the nuclei "feel" only the average value of the energy of the dipole–dipole interaction, which is equal to zero when the specimen is rotated at the magic angle. This leads to a marked decrease in the line width. On the other hand, as shown in Ref.13, the second moment of the spectrum remains unchanged when the specimen is rotated at the magic angle. As a result, the spectrum consists of a narrow central line and a system of side bands separated from it by distances which are multiples of the frequency of rotation.

Similarly, rapid rotation at the magic angle also averages the anisotropy of the chemical shift, giving an isotropic spectrum with an average value $\sigma = 1/3(\sigma_{zz} + \sigma_{yy} + \sigma_{xx})$.

The first-order quadrupole interaction is also effectively averaged when the specimen is rotated at the magic angle.[15] In contrast to this, the second-order quadrupole interaction is not completely averaged when the specimen is rotated in this way. In a number of cases this makes it difficult to obtain well resolved spectra.

The influence of molecular motion on the efficiency of the decrease in the line width as a result of rotation of the specimen at the magic angle has been studied.[17] The possibility of decreasing the line width depends on the type of molecular motion. If there is rapid restricted motion, for example random reorientation of the molecules or individual functional groups about a single axis, there is a partial decrease in the line width, and rapid rotation at the magic angle averages the remaining broadening. If however the molecular motion is completely random, but its rate is not sufficient to give narrow lines with widths close to the line widths in the spectra of liquids, then rotation of the specimen with a frequency of several kilohertz does not lead to a decrease in the line width. A decrease in width takes place if the frequency of the rotation is higher than the frequency of the molecular motion, which in most cases cannot be achieved in practice. This limitation in the production of high-resolution spectra also applies to other methods for decreasing the line widths in the spectra of solids.[2-5]

*b) Multi-pulse sequences*

In the case of very strong dipole interactions, when rotation of the specimen at the magic angle at attainable rates gives no result, the line width can be decreased using multi-pulse sequences.[2-5] In a multi-phase experiment, a four-pulse cycle is usually employed.[5] As a result, the average values of the Hamiltonians of the dipole and quadrupole interactions become zero. When a sequence of radiofrequency pulses is applied to a spin system, the nuclear spins begin to rotate about an axis making the magic angle with the direction of the field, and in the rotating system of coordinates the vector of the magnetisation of the system is oriented at this angle to the external field. As a result, the dipole–dipole interactions disappear. The Hamiltonian of the dipole interaction (2) can be represented as:

$$\mathcal{H}_D = \sum_{i<j} \gamma_i\gamma_j\hbar^2 r_{ij}^{-5}(\vec{r}_{ij}\vec{r}_{ij} - 3z_{ij}z_{ij})\,[\vec{\mu}_i\vec{\mu}_j - 3\,(\mu_z)_i\,(\mu_z)_j] \qquad (5)$$

In expression (5) the dependence of $\mathcal{H}_D$ on the coordinates of the vector $\vec{r}_{ij}$ and its dependence on the orientation of the spin moments are identical, so that rotation of the specimen and rotation of the nuclear spins at the same angle to the direction of the field lead to the same result.

The application of an appropriately selected sequence of radiofrequency pulses can reduce to zero not only the dipole–dipole interaction but also the first-order quadrupole interaction.[5] The effects of the chemical shift are preserved, although they are decreased by a factor of $3^{1/2}$, since the projection of the magnetisation vector on the direction of the external field is reduced by this factor. The spin–spin interaction via the chemical bond, which is independent of the magnitude of the angle, remains unchanged. Thus a sequence of radiofrequency pulses can be used to obtain high-resolution NMR spectra for solid specimens.

The efficiency of the decrease in the line width in multi-pulse experiments depends to a marked extent on the accuracy of the tuning of the pulses. Such factors as the finite length of the pulses, the non-uniformity of the radiofrequency field, the inaccuracy of the tuning of the phases, and the distortion of the form of the pulses have a marked influence on the width of the spectra obtained. These difficulties can be partly overcome by using complex sequences.[18,19] Almost all more complex pulse sequences are based on the four-pulse sequence in such a way that the experimental errors do not accumulate from one cycle to another.

The influence of various factors on the effective line width in multi-pulse experiments has been analysed;[18,19] it has been shown that the form of the high-resolution spectrum depends to a marked extent on the conditions of the experiment and even on the actual magnitude of the chemical shift. This may make it difficult to interpret the spectra and to determine the components of the shielding tensor. Another problem is that multi-pulse experiments do not completely eliminate heteronuclear dipole interactions, that is interactions between nuclei of different types. Like the anisotropy of the chemical shift, the heteronuclear dipole interaction decreases by a factor of $3^{1/2}$ in a four-pulse experiment. To suppress this interaction, it is necessary to use methods based on double resonance, for example cross polarisation.

*c) Cross polarisation*

Cross polarisation[20] is most widely used to obtain high-resolution spectra for $^{13}C$ nuclei. The method not only suppresses dipole interactions but also increases the intensity of the $^{13}C$ NMR signals by a factor of ~4 as a result of the transfer of polarisation from protons to carbon nuclei.

The first experiments to record NMR spectra using cross polarisation were described in Refs. 21 and 22. The method was subsequently improved considerably,[20] when it was shown experimentally that it is possible to suppress the scalar spin–spin and dipole interactions between spins of two kinds ($I_1$ and $I_2$) by recording the NMR spectrum of the spins $I_1$ under conditions in which the spins $I_2$ are irradiated by a strong electromagnetic field whose frequency is equal to their Larmor frequency. Under these conditions, not only are the scalar and dipole interactions between the spins $I_1$ and $I_2$ suppressed, but the relaxation time for the nuclear spins $I_1$ may also be decreased as a result of the exchange of energy between them. The recording time of the spectrum of the nuclei $I_1$ is preserved, so that the sensitivity of the method is increased as a result of accumulation of the signal.

In cross polarisation experiments, the scalar spin–spin and dipole interactions are completely suppressed, whereas the anisotropy of the chemical shift remains unchanged, so that it can be studied in pure form. As a rule, for $^{13}C$ nuclei the difference between the components of the chemical shift tensor reaches several hundred p.p.m. As a result, the spectrum is extended considerably over a wide frequency range. In this case it is possible to use a combination of cross polarisation and rotation of the specimen at the magic angle. This method often makes it possible to obtain for solid specimens spectra whose resolution is comparable with that of the spectra of liquids.

Thus special methods (rotation of the specimen at the magic angle, multi-pulse sequences, and cross polarisation) can suppress the interactions leading to line broadening and hence give high-resolution spectra for solids. The suppression of second-order quadrupole interactions presents the greatest difficulties. Here, the principal method involves increasing the resonance frequency by using stronger magnetic fields. It is also possible to use a method based on the recording of many-quantum transitions between levels which are not influenced by first-order quadrupole effects.[23-27] Dipole–dipole interactions can be suppressed fairly frequently by the above methods involving rotation at the magic angle, multi-pulse sequences, and cross polarisation.

## III. THE STUDY OF HETEROGENEOUS CATALYSTS

This section examines the results of the study of the structure of heterogeneous catalysts and their active centres by NMR involving the nuclei of different elements and the methods for decreasing the line width described in the previous section.

### 1. The $^{51}V$, $^{17}O$, and $^{23}Na$ NMR Study of Vanadium Catalysts for the Oxidation of Sulphur Dioxide

Oxygen-containing compounds of vanadium form part of many industrially important oxidation catalysts. The structure of the active centres and the mechanisms of the action of these catalysts have been insufficiently studied, however. The present section demonstrates for the example of catalysts for the oxidation of sulphur dioxide the possibilities provided by NMR using the nuclei of $^{51}V$ (natural abundance ~100%) and various other elements in the study of the structure and mechanisms of the production of vanadium catalysts.

The catalysts used to oxidise sulphur dioxide are sulphate and pyrosulphate compounds of vanadium and alkali metals, deposited on a porous carrier, usually silica gel or an aluminosilicate. X-Ray diffraction has shown that in these compounds, vanadium is surrounded by oxygen atoms forming a regular or distorted tetrahedron or a distorted octahedron.

$^{51}V$ NMR spectra recorded at low frequencies usually have a very complex form, because of the simultaneous influence of dipole and quadrupole interactions and chemical shift effects, which may be of the same order of magnitude.[28] On going to high resonance frequences $\nu_0 \cong 79$ MHz, achieved by using magnets with a field $H_0 \cong 7$ T, however, the influence of second-order quadrupole effects becomes insignificant, the spectra become much simpler, and it becomes possible to measure the anisotropy of the chemical shift.

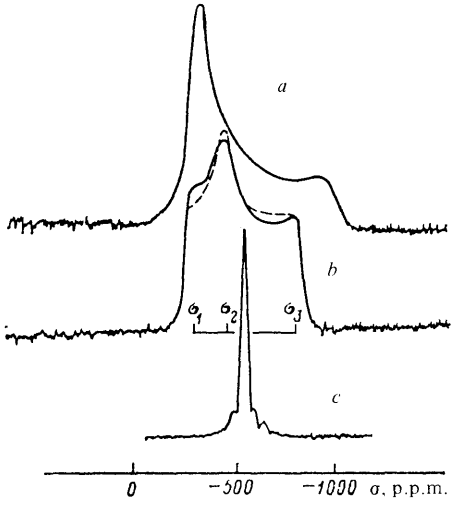



Figure 1. $^{51}V$ NMR spectra of vanadium compounds with different oxygen environments; the chemical shifts are given relative to $VOCl_3$;[29] *a*) $V_2O_5$ (distorted octahedron), *b*) $KVO_3$ (distorted tetrahedron), *c*) $K_3VO_4$ (regular tetrahedron).

The spectra of a number of individual vanadium compounds with known structures were studied first,[29] and it was shown for a large number of these model compounds that the anisotropy of the chemical shift can be taken as a characteristic of the structure of the oxygen environment of the vanadium atoms. Fig.1 shows typical $^{51}V$ NMR spectra for vanadium atoms in a regular tetrahedral environment (orthovanadates and pyrovanadates), in a distorted tetrahedral environment (metavanadates), and in a bipyramidal (distorted octahedral) environment (vanadium pentoxide, sulphate vanadates). For ortho- and pyrovanadates, the spectrum is almost isotropic. The spectrum of metavanadates indicates triaxial anisotropy of the chemical shift tensor (the corresponding spectrum, obtained by calculation using the optimally selected values of $\sigma_1$, $\sigma_2$, and $\sigma_3$, is given by the broken line in Fig.1). Vanadium in a bipyramidal environment gives spectra with almost axial symmetry of the tensor $\sigma$. For alkali metal metavanadates, a correlation is observed between the anisotropy of the chemical shift and the degree of distortion of the tetrahedron.[29]

The $^{51}V$ NMR spectra of different industrial catalysts for the oxidation of $SO_2$ (KS, BAV, and IK-1 grades) before the catalytic reaction differ considerably and depend on the method used to prepare the catalyst. Treatment of the catalysts under the conditions of the catalytic reaction, however, smooths out these differences to a considerable extent.[30] Thus in all the catalysts studied, the active component is produced in the course of the actual catalytic reaction. Although the chemical character of the compounds responsible for the catalytic properties of vanadium catalysts has not yet been finally determined, some preliminary conclusions can be reached. Thus comparison of the $^{51}V$ NMR spectra of the catalysts with the spectra of sulphate vanadates (see Fig.2) shows that one of the principal components of the industrial catalysts is the sulphate vanadate $K_3VO_2SO_4S_2O_7$.

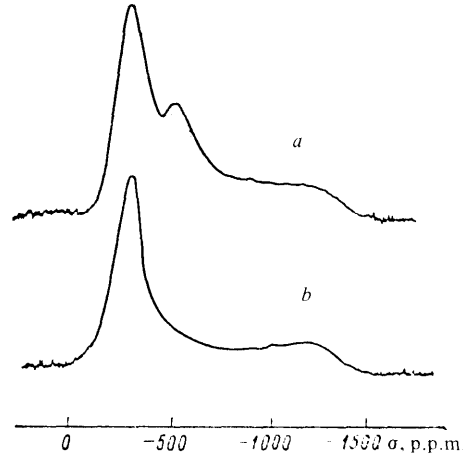



Figure 2. Comparison of the spectrum of the IK-1 catalyst for the oxidation of sulphur dioxide (*a*) with that of the potassium sulphate vanadate $K_3VO_2SO_4S_2O_7$ (*b*); the chemical shifts are given relative to $VOCl_3$.[31]

In addition to the lines from potassium sulphate vanadate, the spectra of the industrial catalysts usually show a line with $\sigma \cong -500$ p.p.m. relative to $VOCl_3$, characteristic of vanadium atoms in a regular tetrahedral environment (see Fig.2). This line has been assigned to vanadium atoms interacting with the carrier, silica gel or an aluminosilicate.[31] Thus vanadium pentoxide deposited on silica gel gave the same line;[31] its intensity increased with increase in the surface area of the silica gel for a constant quantity of vanadium pentoxide. Thus the carrier reacts chemically with the active component. Reactions of this type may be responsible for the fact that the catalytic activity depends on the type of carrier.

The spectra in Figs.1 and 2 were recorded at room temperature, at which the active component of the catalysts and the model compounds are solid. Under the conditions of the oxidation of sulphur dioxide (400–500 °C), however, the active component of the catalysts is in the molten state, and forms a very thin liquid film on the solid carrier. The chemical composition of the catalysts cooled to room temperature may differ from the composition at a high temperature. The spectra of the vanadium catalysts were therefore studied at 500 °C in an atmosphere of the reaction medium.[32]

The $^{51}V$ NMR spectra could not be observed at this temperature, because of the large width, apparently due to the short spin–lattice relaxation time of the vanadium nuclei. The melts were therefore studied by $^{17}O$ and $^{23}Na$ NMR. Fig. 3 gives the concentration dependence of the chemical shift and the line width for the $^{17}O$ NMR spectrum of vanadium pentoxide–potassium pyrosulphate melts, kept for a long time at 500 °C in an atmosphere of the equilibrium mixture $SO_3 \rightleftarrows SO_2 + \frac{1}{2}O_2$ at an $SO_3$ pressure of 400 mmHg.[32] The chemical shift and the line width depend markedly on the concentration of vanadium in the melt. This shows that a coordinate bond is formed between the pyrosulphate or sulphate anions and the vanadium cations. The nature of the relationships in Fig. 3 can be explained if it is assumed that in the melt there is exchange between sulphate and pyrosulphate anions not combined with vanadium and anions forming a coordinate bond with vanadium. The change in the slope of the lines in Fig. 3 at a vanadium concentration of ~1 M reflects a change in the state of the vanadium complexes, possibly as a result of their dimerisation.

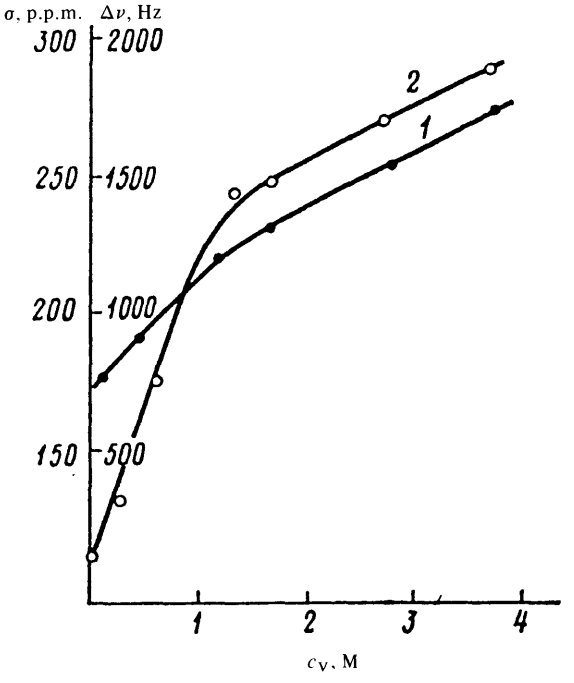



**Figure 3.** Dependence of the chemical shift σ (*1*) and the line width Δν (*2*) of the $^{17}O$ NMR spectra of the $K_2S_2O_7$–$V_2O_5$ system (500 °C, $SO_3$, $SO_2$, $O_2$ atmosphere) on the vanadium concentration; the chemical shift was measured relative to $H_2O$ at 25 °C.[32]

The replacement of potassium by sodium makes it possible to study the $^{23}Na$ NMR spectra of these melts.[32] Fig. 4 gives as a typical example the dependence of the $^{23}Na$ chemical shift on the ratio of the concentrations of sodium and vanadium, obtained for vanadium pentoxide–sodium pyrosulphate melts at 500 °C. These data indicate that sulphate (or pyrosulphate) compounds of vanadium are coordinated to some of the sodium cations. The relatively small changes in σ and the small line width (~300 Hz) agree satisfactorily with the model of outer-sphere coordination of the sodium ions.

Thus the study of vanadium catalysts for the oxidation of $SO_2$ shows that $^{51}V$ NMR can be used successfully to identify the vanadium compounds in heterogeneous catalysts and to detect chemical interaction between the active component and the carrier. $^{17}O$ NMR, even at the natural concentration of this isotope (0.037%), makes it possible to study melts of the active component of the catalyst directly under the conditions of the catalytic reaction.

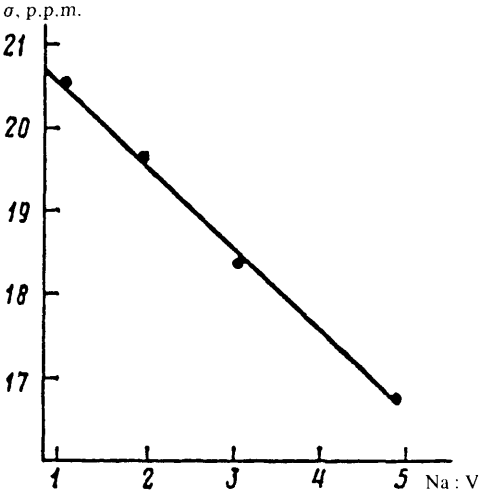



**Figure 4.** Dependence of σ on the ratio Na : V for an $Na_2S_2O_7$–$V_2O_5$ melt at 500 °C; the chemical shift was measured relative to NaCl.[32]

### 2. $^{27}Al$ NMR Studies of the State of Aluminium in Aluminium Oxides and Zeolites

Aluminium in an oxygen atom environment is present in many industrial catalysts. There is good evidence that it is often present in their active centres. The study of the state of aluminium in catalysts from the $^{27}Al$ (natural abundance 100%) NMR spectra is therefore of undoubted interest.

The spin of the $^{27}Al$ nucleus is 5/2. The $^{27}Al$ NMR spectra of powders usually show only the line from the central transition ($1/2 \leftrightarrow -1/2$), whose position is determined by the chemical shift and the second-order quadrupole effect. With increase in the working frequency ($\nu_0$), the chemical shifts increase in direct proportion to $\nu_0$, and the second-order quadrupole shifts decrease in inverse proportion to $\nu_0$. For example, for powdered zeolites and crystalline aluminium oxides even at $\nu_0 \cong 78$ MHz (magnetic field 7 T), the second-order shifts are much smaller than the line widths and the typical chemical shifts produced as a result of a change in the symmetry of the oxygen environment of the aluminium ions. The chemical shifts of aluminium in tetrahedral and octahedral oxygen environments in solution differ by 80 p.p.m.[33] For solids, the magnitude of σ also characterises the coordination state of aluminium, whereas the quadrupole coupling constant depends little on the aluminium coordination (oxygen tetrahedra or octahedra).[34] When the specimens are rotated at the magic angle, it is possible to obtain high-resolution $^{27}Al$

NMR spectra and to observe separately in these spectra the lines from aluminium in tetrahedral and octahedral oxygen environments. Methods for analysing the high-resolution NMR spectra for nuclei with a quadrupole moment have been developed,[35-38] and the principal methods for extracting the spectral parameters from the spectra of nuclei with a spin $I > 1/2$ have been described.

The review of the results of the study of the state of aluminium in heterogeneous catalysts by $^{27}Al$ NMR can begin with an examination of aluminium oxides.[39] Fig. 5 gives the spectra of powdered specimens of different crystalline aluminium oxides, and shows that rotation of the specimens at the magic angle leads to a marked decrease in the line width. For example, for $\gamma$-alumina the line width decreases by a factor of 6, and the two lines corresponding to tetrahedral and octahedral coordination of the aluminium atoms are resolved. Comparison of their positions with those of the lines for model oxygen-containing compounds of aluminium makes it possible to assign the weak-field line to aluminium atoms in a tetrahedral oxygen environment, and the strong-field line to atoms in an octahedral environment. This assignment is confirmed by the spectrum of $\alpha$-alumina, which, as expected from the known structure of this compound, consists of a single line whose chemical shift corresponds to that of aluminium atoms in octahedral coordination. The comparatively good resolution of the spectra makes it possible in principle to determine the relative concentrations of aluminium in octahedral and tetrahedral oxygen environments. Accurate quantitative measurements are difficult, however, since the rotation of the specimens leads to the appearance of side bands which partly overlap the line from the "tetrahedral" aluminium atoms. The side bands are marked with asterisks in Fig. 5.

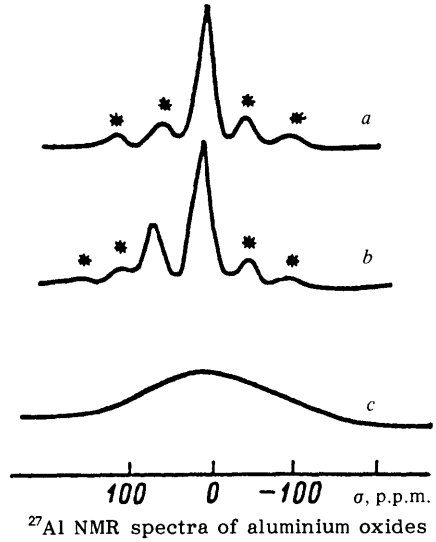



**Figure 5.** $^{27}Al$ NMR spectra of aluminium oxides with rotation of the specimen at the magic angle: *a*) $\alpha$-$Al_2O_3$, *b*) $\gamma$-$Al_2O_3$; *c*) $\gamma$-$Al_2O_3$ without rotation; the chemical shift was measured relative to $Al(H_2O)_6^{3+}$.[39]

In the case of zeolites, the lines from aluminium atoms in tetrahedral and octahedral oxygen environments can be resolved even without rotating the specimens at the magic angle.[30] The $^{27}Al$ NMR spectra[30] show that on hydrothermal treatment of $NH_4Y$ zeolite, which gives HY zeolite, some of the aluminium ions leave their tetrahedral positions in the zeolite lattice and move into cavities where they acquire octahedral coordination. Treatment of the specimens at a high temperature leads to breakdown of the zeolite structure, and a broad line appears in the spectrum.

Measurements of the integral intensity of the $^{27}Al$ NMR spectra have made it possible to determine the relative numbers of aluminium atoms remaining in the lattices of zeolites of types A and Y and displaced into cavities as a result of different forms of hydrothermal treatment and subsequent dehydration of the zeolites.[40,41] The zeolite specimens were placed in a solution of acetylacetone in ethanol, and the intensity of the broad signal from the aluminium atoms remaining in the lattice was compared with that of the narrow signal from the mobile aluminium atoms in the cavities. It was found that only a small proportion of the aluminium atoms (~10%) is displaced from the lattice when the specimens are treated in a shallow bed. When the specimens are treated in a deep bed, the number of aluminium atoms displaced from the lattice increases with increase in temperature. Thus after treatment of the specimens at 400 °C in a deep bed, ~50% of the aluminium atoms were displaced from the lattice. The high-resolution $^{27}Al$ spectra of zeolites which had been rehydrated after hydrothermal treatment and dehydration contained an additional line from the atoms of mobile hydrated aluminium displaced from the lattice. The proportion of this form of aluminium amounted to 70% of the total aluminium displaced from the zeolite framework after treatment at 300 °C. Increase in the temperature of treatment to 700 °C lowered this fraction to 3%. Comparison of the intensity of the $^{27}Al$ NMR lines with that of the $^{1}H$ NMR signals from the OH groups after treatment of the catalysts at different temperatures shows that the zeolite dehydroxylation scheme[42] which assumes that three-coordinate aluminium is formed is incorrect. In fact, dehydroxylation in water vapour takes place at the same time as the removal of aluminium.[40]

Comparison of the $^{27}Al$ NMR spectra of A, X, and Y zeolites established that the A zeolite does not contain Al–O–Al bonds; this confirmed that A zeolite obeys Loewenstein's rule.[43]

Thus the study of the high-resolution $^{27}Al$ spectra makes it possible to determine the coordination state of aluminium in oxides and zeolites and to follow the process of the removal of aluminium from zeolites. Further increase in the working frequency of the spectrometers should make it possible to use the $^{27}Al$ NMR spectra to distinguish tetrahedral aluminium atoms occupying different positions in a zeolite structure.

### 3. $^{29}Si$ NMR Studies of the State of Silicon in Silicate Systems

Silicon oxides, like aluminium oxides, are widely used in heterogeneous catalysis. The $^{29}Si$ isotope (natural abundance 4.7%) has a nuclear spin $I = 1/2$. There are therefore no quadrupole effects in $^{29}Si$ NMR spectra, so that it is usually simpler to obtain high-resolution NMR spectra of solid specimens for $^{29}Si$ nuclei, than for $^{27}Al$ nuclei.

One of the first applications of $^{29}Si$ NMR to the study of catalysts was an investigation of the surface of silica gel using cross polarisation and rotation of the specimen at the magic angle.[44] The use of these methods made it possible to observe in the spectra of silica gel lines with chemical shifts of −109.3, −99.8, and −90.6 p.p.m. relative to tetramethylsilane (TMS), whose intensities changed to different extents

with the transfer of polarisation from the protons to the silicon nuclei. From a comparison of these spectra with the spectra of silicate solutions, the lines with chemical shifts of −99.8 p.p.m. and −90.6 p.p.m. were assigned to the structures $HOSi(SiO_4)_3$ and $(HO)_2Si(SiO_4)_2$, and the line at −109.3 p.p.m. to $Si(SiO_4)_4$ groups. The first two structures correspond to surface silicon atoms joined to one or two hydroxide groups, and the third corresponds to silicon atoms in the volume. These results show that NMR can be used to distinguish chemically non-equivalent silicon atoms, and also surface and volume silicon atoms, in catalysts.

This approach was subsequently used to study the dehydration and rehydration of silica gel.[45] These processes depend markedly on the relative arrangement of the OH groups; $^{29}Si$ NMR was used to determine the quantity of geminal groups, that is structures of the type $(HO)_2Si(SiO_4)_2$. The results[45] showed that none of the previously proposed models explains all the regular features of the change in the structure of the surface during dehydration and rehydration. It was found that the silica gel surface is non-uniform, and may contain regions with structures resembling the (111) and (100) faces of cristobalite. It was concluded[45] that on regions of both types, the rehydration process is determined by kinetic rather than thermodynamic factors.

The possibilities provided by high-resolution $^{29}Si$ NMR spectroscopy for the determination of the ordering of silicon in silicates with different compositions have been demonstrated.[46] The $^{29}Si$ NMR spectra of the solutions and solids are similar, and depend on the condensation of the $SiO_4^{4-}$ tetrahedra. In aluminosilicates, the chemical shifts change regularly with change in the degree of replacement of silicon by aluminium in the tetrahedra closest to the $SiO_4^{4-}$ tetrahedron being considered. The spectra obtained for zeolites of type A showed that each $SiO_4^{4-}$ tetrahedron is surrounded by three $AlO_4^{5-}$ tetrahedra and one $SiO_4^{4-}$ tetrahedron, and that each $AlO_4^{5-}$ tetrahedron is surrounded by three $SiO_4^{4-}$ tetrahedra and one $AlO_4^{5-}$ tetrahedron (3 : 1 ordering). This arrangement of the tetrahedra does not obey the rule of alternation of aluminium–oxygen and silicon–oxygen tetrahedra (Lowenstein's rule,[43] noted above). It was therefore suggested[47] that the previously adopted model of the structure of the A zeolite is incorrect, and neutron diffraction and high-resolution electron microscope data were used to propose a new model for the structure of the A zeolite, containing Al–O–Al bonds.[47] This raised the question of the extent to which Loewenstein's rule can be used to analyse the distribution of aluminium in other zeolites.[48] Suggestions have been put forward on the possible reasons for the breakdown of this rule.

Subsequently, a more detailed study of the NMR spectra of ZK-4 zeolites, in which the aluminium atoms, as in the A zeolite, are present in double four-membered rings, showed that the $^{29}Si$ NMR spectrum depends not only on the number of neighbouring $AlO_4^{5-}$ groups but also on the Si–O–Si or Si–O–Al angle.[49] It was found that the strain of the bonds in structures with four-membered rings, which contain almost linear Si–O–Al bonds, leads to a displacement of the resonance compared with other structures with the same chemical composition. As a result, the signals which were previously assigned to Si atoms having three Al atoms in the second coordination sphere were found to belong to an Si atom joined to four Al atoms in neighbouring tetrahedra, as should be the case for a zeolite A structure obeying Loewenstein's rule.

The distribution of aluminium in X and Y zeolites has been studied in detail,[50,51] and it has been shown that the regular features of the change in the intensities of the lines in the $^{29}Si$ NMR spectra with change in the aluminium concentration obey Loewenstein's rule.

$^{29}Si$ NMR spectroscopy has been used[30,52] to study the displacement of aluminium atoms from the framework of zeolites of type Y on hydrothermal treatment. The high-resolution spectra of specimens from which aluminium ions have been displaced consist of four lines with $\sigma$ from −85 p.p.m. to −105 p.p.m. relative to TMS.[30] According to Ref.46, these lines correspond to Si atoms having 3, 2, 1, and 0 Al atoms in the second coordination sphere. Removal of ammonium ions from the zeolite leads to an increase in the intensity of the lines corresponding to the Si atoms with a smaller number of Al atoms in the second coordination sphere, and to a decrease in the intensity of the lines corresponding to a larger number of Al atoms in the second coordination sphere. This behaviour of the $^{29}Si$ NMR spectra confirms the displacement of the aluminium atoms from the zeolite lattice, detected from the $^{27}Al$ NMR spectra (see previous section).[30,52]

The $^{29}Si$ NMR spectra of Y zeolites from which aluminium ions had been displaced by thermochemical treatment in the presence of water vapour have been studied.[53] The spectra were used to calculate the concentration of $Si(O_4Si)_{4-n} \cdot (O_4Al)_n$ groups. The results show that the rate of the removal of aluminium increases with increase in the degree of replacement of $Na^+$ by $NH_4^+$ in the original specimens, and also with increase in the temperature of treatment and the partial pressure of water vapour.

The distribution of aluminium and silicon in the lattices of zeolites from which aluminium has been displaced influences their catalytic activity, adsorbing power, acidity, stability, etc. If the displacement of aluminium takes place at a sufficiently high temperature, the distribution of silicon and aluminium depends chiefly on the final ratio of the numbers of Si and Al atoms in the lattice, and not on the conditions and type of process involved in the displacement of aluminium.[54] For a given Si/Al ratio, the aluminium distribution was the same in zeolites obtained by direct synthesis and in specimens obtained by displacing aluminium, which had a higher initial aluminium concentration. Thus the final distribution of silicon and aluminium is not sensitive to the conditions of preparation of the specimen, and is determined by the minimum energy of the entire lattice. This indicates that there is a redistribution of the Si and Al atoms in the zeolite during the displacement of aluminium. If however the displacement of aluminium is carried out at relatively low temperatures, the lattice vacancies formed by the displacement of Al atoms are not occupied by Si atoms, and close to these vacancies there are four hydroxide groups (apparently one OH group next to each of the four neighbouring Si atoms). This follows from cross-polarisation experiments which showed an increase in the strength of the signals from Si atoms having one neighbouring OH group.[55]

The $^{29}Si$ NMR spectra have been used[56] to study the state of silicon in the lattices of ZSM-5 and ZSM-11 zeolites with different aluminium concentrations (the Si/Al ratio was varied from 30 to 1000). The line with $\sigma = -105$ p.p.m. was assigned to Si atoms joined to one Al atom in the second coordination sphere, since the intensity of this line decreased with decrease in the quantity of aluminium in the zeolites. The intensity of the line with $\sigma = -115$ p.p.m. in the spectra of the ZSM-11 zeolites was double that for the ZSM-5 zeolites. This made it possible to assign this line to Si atoms in four-membered rings, since the unit cell of the ZSM-5 zeolite contains four four-membered rings, and the unit cell of the ZSM-11 zeolite contains eight four-membered rings. The line with $\sigma = -103$ p.p.m. in the spectra of the ZSM-11 zeolites was assigned to silanol groups Si–OH. It was suggested[56] that the replacement of silicon by aluminium in these zeolites takes place in five-membered rings.

Thus high-resolution $^{29}Si$ NMR spectroscopy makes it possible to distinguish and identify different states of silicon in silicate structures, to obtain data on the distribution of silicon in zeolites, and to study surface Si atoms in silica gel and zeolites.

### 4. $^{195}Pt$ NMR Studies of Deposited Platinum

Since catalysts based on platinum are widely used in many industrial processes, the first papers on the use of $^{195}Pt$ NMR to study highly dispersed platinum deposited on aluminium oxide[57–59] are of considerable interest.

The $^{195}Pt$ nucleus (natural abundance 33%, spin 1/2) has the greatest Knight shift (3.37%) among metals, and this makes it possible to observe separately the signals from surface platinum atoms bonded to the carrier or to adsorbed molecules and from metallic platinum atoms in the volume. The very wide range of values of $\sigma$, the appreciable anisotropy of the chemical shift tensor, and the existence of platinum in a number of states on the surface are responsible for the appearance in the spectrum of a broad line from surface platinum atoms (~0.45 T). This is approximately $10^3$ times the typical line width in the spectra of solids. These exceptionally broad and therefore low-intensity lines have been recorded by accumulating the spin echo signals at a constant frequency with a gradual change in the magnetic field. Specimens with a platinum concentration of ~10% containing platinum particles with different dimensions were studied.[57] It was found that the form of the NMR line depends markedly on the average size of the particles and is sensitive to chemical treatment of the platinum surface. The spin–spin and spin–lattice relaxation times $T_1$ and $T_2$ changed on going from one region of the spectrum to another, but were the same for a given value of the magnetic field and for a given type of treatment of the surface, irrespective of the degree of dispersion of the specimens. The specimen with the largest platinum particles gave a narrow peak from metallic platinum.[57,58] After the specimens were treated with hydrogen or air, the spectra showed an intense peak with a chemical shift characteristic of diamagnetic platinum compounds. This peak was assigned to surface Pt atoms chemically combined with hydrogen or oxygen. Evidence in support of this assignment was provided by the long (~0.1 s) relaxation time $T_1$, whose dependence on temperature and on the field was different from that for metals.

For specimens of highly dispersed platinum on aluminium oxide after the chemisorption of carbon monoxide, the use of $^{13}C$ and $^{195}Pt$ double resonance made it possible to distinguish the signals from the Pt atoms in the surface layer and in the volume.[59] This is possible since irradiation of the specimen at the $^{13}C$ resonance frequency influences only the spectrum of those Pt atoms which are in direct proximity to C atoms. It was found that the magnitude of the spin–spin coupling constant between the carbon and platinum nuclei is similar to that of the corresponding constant for diamagnetic platinum carbonyl molecules. Thus carbon monoxide is bonded to deposited platinum through the carbon atom, as in platinum carbonyls.

### 5. $^{17}O$ NMR Studies of Oxides

Since oxide compounds are widely used as catalysts, the possibility of studying them by $^{17}O$ NMR is of considerable interest. The only oxygen isotope with a non-zero magnetic moment, $^{17}O$, has a very low natural abundance (0.037%). Until recently, therefore, $^{17}O$ NMR spectroscopic studies were carried out only for solutions and mainly using enriched specimens, and there were no published data on the $^{17}O$ NMR of crystalline specimens. Increase in the sensitivity of the method has made it possible to carry out routine measurements of the $^{17}O$ NMR spectra of solutions and to begin the $^{17}O$ NMR study of solid oxides.

The $^{17}O$ NMR spectra of MgO and $Ni_xMg_{1-x}O$ solid solutions with the natural concentration of the $^{17}O$ isotope were first reported in Ref.60. The chemical shift for oxygen in MgO was measured, and it was shown that the NMR parameters (line width, spin–lattice relaxation time) can be used to analyse the distribution of the paramagnetic $Ni^{2+}$ ions in the MgO lattice. In the analysis of enriched (enrichment in $^{17}O$ up to 20%) specimens of MgO, $SiO_2$, $\alpha$-$Al_2O_3$, and $CaMg.Si_2O_6$ [61] it was possible, using rotation at the magic angle, to resolve lines from structurally non-equivalent O atoms in the NMR spectra. Thus the spectrum of $CaMgSi_2O_6$ showed three lines from non-equivalent O atoms, whereas the $^{29}Si$ spectrum consisted of only a single line. The fact that the $^{17}O$ nucleus has a quadrupole moment makes it possible to obtain additional information on the symmetry of the environment of oxygen in the lattice by studying the quadrupole effects in the NMR spectra.

Thus the first studies of the $^{17}O$ NMR spectra of solid oxides demonstrate the possibilities provided by the method for structural studies based on the measurement of both the chemical shifts and the parameters of the quadrupole interaction.

### 6. $^{1}H$ NMR Studies of Surface OH Groups

The structure of the hydroxide covering of catalyst surfaces plays an important role in heterogeneous catalytic processes, so that it has been studied intensively by many methods, chiefly infrared spectroscopy.[62] A large number of studies have also been carried out by the traditional versions of NMR.[2] The use of the methods for decreasing the NMR line width makes it possible to observe separate lines from hydroxide protons of different chemical character, and this opens up the possibility of finding the relationship between the proton-donor properties of hydroxide groups and the nature of their chemical bond with the surface.

Thus the first papers[63,64] on the use of multi-phase sequences to study the OH groups of silica gel and aluminosilicates showed that this technique makes it possible to decrease the width and to measure the components of the tensor of the chemical shift for OH groups. For aluminosilicates, the free induction signal consisted of two components, one of which decreased more rapidly, and the other more slowly; the first component was assigned to OH groups bonded to aluminium, and the second to Si–OH groups. This made it possible to determine quantitatively the concentrations of OH groups of different types.

The proton resonance spectra of A-300 Aerosil dehydrated in a vacuum, with rotation at the magic angle, showed two lines with $\sigma$ = 2.0 p.p.m. and 2.9 p.p.m., corresponding to Si–OH and $Si(OH)_2$ groups respectively.[65] This made it possible to determine the concentrations of both types of group. When the specimen was kept in moist air, the spectrum showed new lines of two types, assigned[65] to water in hexagonal pores (signal with $\sigma$ = 1.1 p.p.m.) and water forming hydrogen bonds (signal with $\sigma$ in the range 4.2–4.4 p.p.m.).

For hygroscopic adsorbents and catalysts, the spectra of the OH groups are usually recorded in sealed ampoules, since atmospheric moisture adsorbed on the catalyst surface may distort the results considerably. The first studies of the NMR spectra of OH groups with rotation of the specimens

at the magic angle in sealed ampoules were described in Ref. 66. For silica gel it was possible to obtain a line width of 170 Hz, but the width was greater for the other specimens (~900 Hz for zeolites).

In the NMR spectra of the OH groups of HZSM-5 zeolites with different Si/Al ratios[68] without rotation of the specimen, the line width was ~4 kHz. With rotation of the specimen, the line width decreased by a factor of 6; this made it possible to resolve in the spectrum two lines with $\sigma = 1.4$ p.p.m. and 4.3 p.p.m. Since the intensity of the signal with $\sigma = 4.3$ p.p.m. increased with increase in the concentration of aluminium in the zeolite, this line was assigned to OH groups chemically combined with aluminium. The line with $\sigma = 1.4$ p.p.m. was assigned to Si–OH groups; this conclusion was confirmed by the fact that in the spectrum of silica gel the OH groups gave almost the same value of $\sigma$ (1.7 p.p.m.).[68] The spectra of amorphous aluminosilicates, including those of specimens with the same aluminium concentration as the HZSM-5 zeolites, did not show a line with $\sigma = 4.3$ p.p.m., corresponding to hydroxide groups joined to aluminium. This indicates that the concentration of these OH groups in zeolites is much higher than in amorphous aluminosilicates with the same composition. Phosphate catalysts contain several hydroxide groups of different types: P–OH and E–OH, where E is the second element in the phosphate. The lines with $\sigma$ in the range 3.1–4.4 p.p.m. are assigned to P–OH groups; the spectra of some specimens show lines due to P–OH groups forming a hydrogen bond, which displaces the signal of the OH groups to weak fields (the lines with $\sigma =$ 5.7 p.p.m. and 8 p.p.m. for $BPO_4$ and 5.8 p.p.m. for tin phosphate). The greatest shielding of the protons ($\sigma = -0.3$ p.p.m.) is observed for calcium phosphate; this possibly reflects the highly basic nature of the Ca–OH groups.

Comparison of the chemical shifts of the OH groups and the charges on the protons.

| OH group | $\sigma$, p.p.m. | $q$, e (Ref.68) | OH group | $\sigma$, p.p.m. | $q$, e (Ref.68) |
|---|---|---|---|---|---|
| $H^+$ ion in the gas phase | 31 (Ref.67) | 0.0 | Si–OH | 1.7 | 0.72 |
| P–OH | 3.1 | 0.7 | Al–OH | 1.2 | 0.76 |
| Al–O(H)–Si | 4.3 | 0.71 | B–OH | 1.1 | 0.76 |

Notation: $\sigma$ is the chemical shift relative to TMS, and $q$ the relative density of the charge on the proton.

The chemical shift in $^1$H NMR spectra is the sum of three components, produced by the effects of the shielding of the protons by the electron cloud (the so-called electronic component), the magnetic anisotropy of the chemical bonds, and the polarisation of the electron clouds by the charges of neighbouring ions. The values of $\sigma$ for OH groups of different kinds have been compared[68] with the values of the charges on the protons of the surface OH groups, calculated by the MINDO/3 method, which usually gives an accurate description of the charge distribution; the results of the comparison are given in the Table. The Table shows that the signal tends to be displaced to a strong field with increase in the negative charge on the proton. This may indicate that the change in the chemical shift is determined to a large extent by the change in the electronic component.

The $^1$H NMR spectra of ZSM-5 zeolites after thermal vacuum treatment at 200 °C and 350 °C have been studied.[69] These specimens contain hydroxide groups of two types; the weak-field signal was assigned to the protons of the Si–O(H)–Al group, and the strong-field signal to the protons of the Si–OH group.

The state of the protons in zeolite cavities has been studied.[70] The proton resonance signal after a $\pi/2$ pulse in hydrated NaA, NaX, and NaY zeolites at room temperature consists of rapidly ($\lesssim 100$ μs) and slowly ($> 1$ ms) damped components. The first component is assigned to the protons in β-cavities (cubo-octahedra); it was not clear whether the protons in these cavities belonged to water molecules or to OH groups. To investigate this question, sodalites, which contain only β-cavities, were studied. For these specimens, the signal contained only the rapidly damped component, and this made possible a more detailed study of the state of the protons in the β-cavities. It was found that the concentration of OH groups was only 0.5 per cubo-octahedron, and that they appear in the initial stage of the hydration of the zeolite after its activation at 400 °C. The number of OH groups does not increase with increase in the degree of filling of the zeolite cavities by water molecules, and is independent of temperature in the range between −150 °C and +150 °C. All the other protons belong to water molecules in the cubo-octahedra (~4 molecules per cubo-octahedron). The study of the temperature dependence of the spectra made it possible to follow the mobility of the water molecules.[70] In the comparatively short temperature range between −150 °C and 0 °C, the molecules undergo rapid anisotropic rotation; at a temperature above 0 °C the rotation becomes isotropic; and above 80–130 °C, translational movement of the water molecules between different cubo-octahedra takes place.

## IV. THE STUDY OF ADSORBED MOLECULES AND THEIR TRANSFORMATIONS

The high-resolution NMR spectra of adsorbed molecules can be obtained using the same methods of decreasing the line width as in the study of catalysts. The use of these methods is often made difficult, however, by the comparatively low concentration of adsorbed molecules. For this reason, in a number of cases, the NMR characteristics of chemisorbed species are obtained by recording the spectra under the conditions of the rapid exchange of molecules between the chemisorption centres and physical adsorption. A similar rapid-exchange procedure is widely used to study the complexes of reagents with metal-complex catalysts.[1] It makes it possible to determine the parameters of the low-intensity NMR spectra of chemisorbed species from the concentration dependence of the parameters of the overall averaged NMR spectrum of chemisorbed and physically adsorbed species. The intensity of this overall spectrum may be increased considerably by the high concentration of physically adsorbed species.

Rapid (on the NMR time scale) exchange between the chemisorbed and physically adsorbed states of molecules is encountered fairly frequently. The characteristic features of the analysis of NMR spectra under these conditions will be examined first, followed by an analysis of the results of NMR studies of specific adsorption and catalytic processes.

### 1. NMR Spectra with the Exchange of Molecules in the Adsorbed Layer

The principles of the analysis of NMR spectra with exchange in the adsorbed layer were developed in Refs.71–76. It is assumed that on a catalyst surface, molecules are present either in the chemisorbed state, which is characterised by a chemical shift $\sigma_A$ and a lifetime $\tau_A$, or in a state of weak physical adsorption with a chemical shift $\sigma_0$ and a lifetime $\tau_0$. It is also assumed that exchange takes place between these two states as a result of thermal motion. For long lifetimes, that is when $\nu_0(\sigma_A - \sigma_0) \gg \tau_A^{-1}$ and $\nu_0(\sigma_A - \sigma_0) \gg \tau_0^{-1}$, where $\nu_0$ is the resonance frequency of the nucleus, the NMR spectrum consists of the superposition of the signals from the two states. For short lifetimes, if the conditions $\nu_0(\sigma_A - \sigma_0) \ll \tau_A^{-1}$ and $\nu_0(\sigma_A - \sigma_0) \ll \tau_0^{-1}$ are fulfilled, an averaged spectrum will be observed, in which the chemical shift is the average for the molecules in the two states.

If the surface has only one type of chemisorption centre and if the number of adsorption centres $N_A$ is much smaller than the total number of molecules on the surface $N$, the expression for the chemical shift $\sigma$ has the form

$$\sigma = \sigma_A \frac{KN_A}{1 + KN} \qquad (6)$$

where $K$ is the complex-formation constant. The measured dependence of $\sigma$ on $N$ can be used to determine $K$ and the product $\sigma_A N_A$.

The chemical shift for a molecule in an adsorbed layer is often measured relative to the position of the line of the same molecule in the gas. In this situation, the interpretation of the results of the measurements is influenced considerably by the choice of the value of the chemical shift $\sigma_0$ in the "free" state. The chemical shifts of the same molecules in liquids and gases differ considerably as a result of intermolecular van der Waals interactions and self-association.[77,78] In the general case, the greatest differences (5 p.p.m.) are observed for the nuclei situated at the periphery of the molecule. The values of the shifts for the gas phase in the $^{13}C$ NMR spectra in the great majority of cases are displaced to a strong field compared with liquids. In the study of the chemisorption of molecules, the value taken for $\sigma_A$ is often the value of the chemical shift for the same molecules on inert carriers (that is carriers with practically no chemisorption centres), for example silica gel. With this choice of the value of $\sigma_0$, it is possible simultaneously to compensate to a considerable extent the influence of the magnetic susceptibility of the catalyst on the magnitude of the chemical shift of the signal of the adsorbed molecules relative to the molecules in the gas. Experiments have shown that the differences in the chemical shifts as a result of the differences in the magnetic susceptibilities of silica gel and the catalyst (if it is diamagnetic) are usually small (~0.5 p.p.m.).

### 2. $^{13}C$ NMR Studies of the Adsorption of Hydrocarbons and CO

The use of the resonance of the $^{13}C$ nucleus (spin 1/2, natural abundance 1.1%) has a number of advantages over proton resonance. $^{13}C$ NMR spectra have a much greater (by a factor of 20–30) range of chemical shift values, that is they are much more sensitive to a change in the electronic state of the molecule. This often makes it possible to observe a change in chemical shifts in $^{13}C$ NMR spectra in cases where a displacement of the lines in the proton resonance spectrum cannot be detected. On the other hand, the magnetic moment of the $^{13}C$ nucleus is smaller by a factor of ~4 than that of the proton. As a result, there is a decrease in the contribution of dipole interaction to the line width. At the same time the dipole interaction between the $^{13}C$ nuclei is small, because of their low natural abundance, and the dipole interaction of these nuclei with protons can be decreased considerably by broad-band suppression of the spin–spin interaction. Thus the $^{13}C$ NMR spectra of adsorbed molecules have a much higher resolution than the $^{1}H$ NMR spectra. This feature has led to the extensive use of $^{13}C$ NMR spectroscopy to study adsorption, in spite of the fact that, because of the low natural abundance, the intensity of the signal from the $^{13}C$ nuclei is smaller by a factor of approximately $1.8 \times 10^{-4}$ than that from the protons, and the relaxation times, which are much greater than those for protons, require long times for the accumulation and recording of the spectra.

The present section describes the results of the study of the adsorption of hydrocarbon and CO molecules by NMR without rotation at the magic angle. This method makes it possible to study comparatively weak forms of adsorption, when the adsorbed molecules are still able to move (movement over the surface or rotation), so that they have comparatively narrow NMR lines.

The first $^{13}C$ NMR spectra of adsorbed molecules were reported in Refs.79 and 80. The $^{13}C$ NMR spectra of adsorbed butenes and various other hydrocarbons have been studied.[79–84] A change in the chemical shifts and relaxation times was observed when butene isomers were adsorbed on zeolites.[80] The direction and magnitude of the shifts indicate that the electrons of the double bond take part in the interaction of the butenes with the surface active centres of the zeolites.

The spectra of toluene adsorbed on zeolites have been obtained.[82] The data on the chemical shifts of toluene and butenes adsorbed on zeolites were compared with the results of CNDO calculations. In the calculations it was assumed that the hydrocarbons interact with the sodium ions or OH groups of the zeolites. Agreement with experiment was not obtained, however, possibly because the quantum-chemical calculations were insufficiently accurate. The interaction of butenes with AgNaX and AgNaY zeolites has been studied,[83] and it was found that the chemical shifts are the same as those for the alkenes in aqueous solutions of silver salts. It was therefore concluded[83] that the butene molecules are adsorbed on the silver cation to form $\pi$-complexes. In Ref. 84, the $^{13}C$ NMR spectra were used for the first time to follow the isomerisation of but-1-ene into but-2-ene. Almost simultaneously, Gay[86] observed the spectra of carbon dioxide, ethylene, dichloroethane, ethanol, acetone, butenes, dimethyl ether, and hexane adsorbed on silica gel. In all cases the resolution of the $^{13}C$ NMR spectra was much better than that of the $^{1}H$ NMR spectra. For some molecules, changes in the chemical shifts (up to several p.p.m.) relative to the gas phase were observed.

$^{13}C$ NMR spectroscopy has been used[87] to study the adsorption of methane, carbon monoxide, acetylene, ethylene, propene, propyne, carbon oxide sulphide, propane, cyclopropane, and isobutane on NaA, NaX, NaY, and AgY zeolites and on silica gel. The influence of traces of iron in the catalysts on the line width of the adsorbed molecules was studied. At an iron concentration of $\sim 10^{-4}$ at.% it was possible to obtain very narrow lines (width ~10 Hz), and this made it possible to determine the changes in the chemical shifts (± 0.05 p.p.m.) and the spin–spin coupling constants (± 0.2 Hz) with a high accuracy. The magnitude of $\sigma$ was independent of the degree of covering. The shifts of the lines on adsorption on zeolites were attributed to interaction with surface centres—alkali metal cations and OH groups.

One of the main reasons for the change in the values of $\sigma$ for molecules in the adsorbed state is considered to be the influence of the electric field of the surface.[87] The decrease in the spin–spin coupling constant indicates an increase in the length of the C–H bonds in ethylene and propene when they are adsorbed on zeolites. Measurement of the temperature dependence of the line width and the spin–lattice relaxation time led to the conclusion that the mobility of the molecules in the adsorbed state is lower on HY zeolites than on NaY zeolites.

The spectra of a number of linear and cyclic alkenes adsorbed on zinc oxides have been studied.[88] For alkenes in whose molecules the double bond is readily accessible for interaction with surface atoms, the magnitude of $\sigma$ indicated that weak $\pi$-complexes are formed. In substituted alkenes there is steric hindrance to the formation of this bond. In Ref.88, as in most early work, the dependence of the chemical shifts on coverage was not studied, so that the conclusions reached about the relative strength of the bonds formed by different alkenes with the active surface centres of zinc oxide (assumed to be $Zn^{2+}$ ions on the surface) require verification.

The adsorption of butenes on silicon and aluminium oxides has been studied;[89] a correlation was observed between the values of $\sigma$ and the quantity of OH groups on the catalyst surface. On the other hand, spectroscopic studies of the adsorption of butenes on silica gel modified with alkali showed that the alkenes interact not only with the OH groups and sodium ions but also with other centres of the silica gel surface, possibly oxygen anions.[90]

The adsorption of formic acid on titanium dioxide has been studied by $^{13}C$ and $^{1}H$ NMR.[91] Appreciable strong-field shifts of the $^{1}H$ NMR lines and weak-field shifts of the $^{13}C$ lines were observed, due to interaction with the surface paramagnetic $Ti^{3+}$ ions. The dependence of the values of $\sigma$ on the degree of covering of the surface, and EPR data on the number of adsorption centres, were used to determine the values of $\sigma_A$ and the spin densities at the protons and carbon nuclei of the surface complex. Quantum-chemical calculations of the transfer of spin density from the $Ti^{3+}$ ion to the $\pi$-orbitals of the adsorbed molecule[91] show that the experimental values of the spin densities are best explained by an adsorption model in which the structure of the formic acid molecule is distorted relative to its state in the gas phase—it loses its planar structure.

The possibility of observing the change in the concentration of each of the reaction products from the $^{13}C$ NMR spectra enables this method to be used to study the kinetics of the transformation of hydrocarbons on catalyst surfaces and to study the intermediate products of the catalytic reactions. It has been possible to follow the kinetics of the isomerisation of but-1-ene on tin–antimony catalysts from the change with time in the intensity of the lines in the $^{13}C$ NMR spectra from all the reaction products.[92] The kinetic data were used to propose a cyclic model of the surface complex whose geometry ensures the transformation of but-1-ene into but-2-ene and the *cis–trans* isomerisation of but-2-ene.

$^{13}C$ NMR has been used[93] to study the mechanism of the conversion of methanol and ethanol into hydrocarbons on ZSM-5 zeolite. Analysis of the $^{13}C$ NMR spectra made it possible to follow the sequence of transformations of the alcohols into hydrocarbons. All intermediate products were identified (ethers, alkenes, aromatic hydrocarbons, cyclic and saturated hydrocarbons) and a reaction scheme was proposed.

Because of the increase in interest in the study of the Fischer–Tropsch synthesis, an increasing number of studies of the mechanism of this reaction by $^{13}C$ NMR are being reported. The forms in which CO is adsorbed, and the nature of the intermediate products of the reaction of CO and $H_2$, have been investigated.

By using carbon monoxide enriched in the $^{13}C$ isotope (~90%), it has been possible to establish the nature of the species formed when CO or a CO + $H_2$ mixture is adsorbed on an $Rh/La_2O_3$ catalyst.[94]

The magnitude of the shift observed for CO adsorbed on $La_2O_3$ (180–250 p.p.m.) is typical of carbon atoms in metal carbonyls or in aldehyde groups; this indicates that carbonyl-like structures are formed. The $^{13}C$ NMR spectra of carbon monoxide adsorbed on $Rh/La_2O_3$ at 20 °C and 150 °C are also typical of carbonyl structures.[94] Heating these specimens to 200 °C leads to the formation of saturated hydrocarbons as a result of the reaction of the carbonyl species with the OH groups of the surface. In a similar experiment with $Rh/SiO_2$, the chief product was ethylene, and the degree of transformation of the carbonyls to the hydrocarbon was much lower than on $Rh/La_2O_3$.

For mixtures with $CO:H_2 = 1:3$ on an $Rh/La_2O_3$ catalyst, the reaction of CO with $H_2$ begins with the formation of carbonyl species with $\sigma$ = 180–150 p.p.m. Up to 80 °C, no other species were detected. Heating at 200 °C leads to the formation of alcohols. At 240 °C, the alcohols are dehydrated to give hydrocarbons (lines at 10–30 p.p.m.), which in turn are converted into methane at 260 °C.[94] At lower partial pressures of hydrogen ($CO:H_2 = 1:1$) and a temperature of 230 °C, large quantities of oxygen-containing compounds with carbonyl groups (lines with $\sigma \cong$ 180–220 p.p.m.) and compounds of the formate type (lines with $\sigma \cong$ 150–180 p.p.m.) are formed. With increase in temperature, saturated hydrocarbons predominate in the reaction products. These examples show that $^{13}C$ NMR can be used to study the intermediate products of the heterogeneous catalytic reactions between CO and $H_2$.

A study of the $^{13}C$ NMR spectra of CO and $CO_2$ adsorbed on zeolites[95] detected unusually large weak-field shifts of the signals (by ~30–80 p.p.m.) compared with gaseous CO. The shifts were observed after zeolite treatment leading to the displacement of aluminium (heating at a high temperature in a deep bed of the specimen); it was therefore concluded that the CO molecules interact with Lewis centres, that is with the aluminium atoms displaced from the zeolite lattice. These effects were not observed for $CO_2$. A model *ab initio* calculation of the interaction of CO with an isolated $Al^{3+}$ ion[96] showed that the potential energy on the surface has two minima, which correspond to the attachment of a CO to an $Al^{3+}$ ion via the carbon atom or via the O atom, with approximately equal stabilisation energies. Comparison of the results of the calculation of the chemical shift tensors with the experimental data led to the conclusion that in the decationated zeolites the addition of CO to $Al^{3+}$ takes place preferentially via the O atom.

A study of the state of CO adsorbed on $Rh/Al_2O_3$[97,98] detected species of two types, which give overlapping $^{13}C$ NMR spectra; these spectra differ, however, in their spin–lattice relaxation times. In this case, NMR supplements the results obtained by infrared spectroscopy (which does not detect two forms of adsorbed CO).

The methods of the high-resolution $^{13}C$ NMR spectroscopy of solids, involving suppression of the dipole interaction with protons, cross polarisation, and rotation of the specimens at the magic angle, are now beginning to be used increasingly to study strongly adsorbed molecules.

$^{13}C$ NMR with cross polarisation and suppression of the dipole and scalar interactions with protons has been used[99] to study the interactions of methanol, toluene, and ethylbenzene with modified zeolites of type X, used as catalysts for the synthesis of styrene. The results[99] show that the

introduction of alkali metal cations (NaX and CsX) leads to a change in the geometry of the zeolite cavities and the composition of the intermediate reaction products. The change in the size of the "windows" in the zeolites with change in the nature of the alkali metal influences the mobility of the adsorbed molecules (revealed by a change in the NMR line width) and the geometry of the intermediate state (revealed by the formation of different intermediate reaction products, detected from the characteristic shifts in the NMR spectra). Thus on NaX zeolite the dehydration of methanol predominates, whereas on CsX zeolite, dehydrogenation predominates. Formaldehyde is converted into dimethyl ether on NaX, and into methanol on CsX.

The chemisorption of methanol on magnesium oxide has been studied by cross polarisation.[100] The $^{13}C$ NMR spectra of adsorbed methanol had axial symmetry. Comparison with the spectra of potassium, calcium, and magnesium methoxides made it possible to assign the lines obtained after the adsorption of 6 μmole $m^{-2}$ methanol to surface magnesium methoxides, firmly bound to the catalyst surface. At high degrees of coverage, mobile methanol molecules joined to OH groups by hydrogen bonds are formed on the surface.

$^{13}C$ NMR has been used[101] to study the conversion of methanol on NaGeX-300 zeolite, which has a structure similar to that of faujasite. The formation of dimethyl ether and partial methoxylation of the surface were detected at 300 °C. In the presence of water, the surface methoxy groups are readily converted into methanol at 25 °C.

Important information can also be obtained by analysing the form of the lines in the $^{13}C$ NMR spectra. In the adsorption of benzene on NaY zeolite, the line width reaches a maximum after the adsorption of four benzene molecules for every large cavity.[102] This was taken[102] as indicating that benzene reacts with four sodium ions in a large cavity.

An analysis of the form of the lines in the spectra of CO, $CO_2$, $CS_2$, and COS adsorbed on zeolites has been used to identify the probable centres on which these molecules are adsorbed in mordenites.[103] This identification can be carried out by studying (from the form of the NMR line) the characteristic features of the movement of the molecules in the zeolites. The molecules have a low mobility if their dimensions and the dimensions of the adsorption sites coincide, and are extremely mobile if the dimensions of the cavities in which adsorption takes place are much greater than the dimensions of the molecules. For example, the data obtained[103] for $CO_2$ adsorbed on Na-mordenite indicate that the zeolite contains molecules of three types: stationary, rotating anisotropically, and rotating isotropically. These results can be attributed to the adsorption of $CO_2$ molecules in three different positions: inside channels formed by large rings, inside channels formed by small rings, and on the external surface respectively. For K-, Cs-, and $NH_4$-mordenites, adsorption of gases in the small channels is not observed. These cations apparently themselves occupy the positions in the small channels, preventing the adsorption of other molecules in them.

### 3. The Use of Rotation at the Magic Angle to Study Adsorbed Molecules

The chief problem arising when rotation at the magic angle is used to study adsorbed molecules is associated with the need to rotate sealed glass ampoules. The strong centrifugal forces produced by rotation at a frequency of 2–4 kHz often lead to rupture of the ampoules. An ampoule and a rotor have been designed[104,105] for carrying out measurements with sealed ampoules at a rotation frequency of 2–2.5 kHz.

The efficiency of rotation of the specimen at the magic angle is illustrated in Fig.6, which gives the $^1H$ NMR spectra of propene adsorbed on $\gamma$-$Al_2O_3$.[104] In experiments without rotation of the specimen, the line width is ~500 Hz, which makes it impossible to resolve the lines from the protons of the CH and $CH_2$ groups. On rotation at the magic angle, the line width decreases by a factor of ~20, all the lines of propene are resolved, and the accuracy of the measurement of $\sigma$ is increased (to ±0.02 p.p.m.). For this system, all the resonance lines of both the $^1H$ NMR spectrum and the $^{13}C$ NMR spectrum are displaced to a weak field, compared with the spectrum of gaseous propene; the largest shift was observed for the CH group.

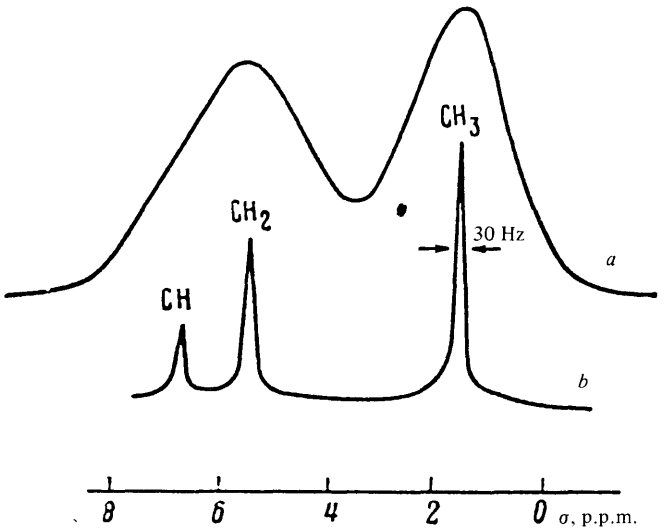



Figure 6. Influence of rotation at the magic angle on the $^1H$ NMR spectra of propene adsorbed on $\gamma$-$Al_2O_3$; the spectra were obtained: *a*) without rotation, *b*) with rotation at a frequency of 2 kHz.[104]

The dependence of the chemical shift on the degree of covering of the $\gamma$-$Al_2O_3$ surface by propene from the $^1H$ and $^{13}C$ NMR spectra is typical of rapid exchange between physically and chemically adsorbed alkene molecules. The dependence is effectively described by Eqn.(6), which corresponds to the chemisorption of propene on an active centre to give a 1:1 complex. Fig.7 gives the dependence of the chemical shift on the quantity of adsorbed propene.[105] The dependence of $\sigma$ on the degree of covering was used to find the complex-formation constant, whose value, as expected, was the same for all six lines in the $^1H$ and $^{13}C$ spectra. The values of the product of the chemical shift of the signal of the molecules in the adsorbed state and the number of chemisorption centres were also calculated. It was found that the complex-formation constant is independent of the temperature of preliminary vacuum treatment, whereas the product $\sigma_A N_A$ for all the lines increases with increase in the temperature of treatment (see Fig.7). This indicates that the propene chemisorption centres are most probably coordinatively unsaturated aluminium ions, the number of which increases with increase in the treatment temperature. A marked decrease in the values of the spin–spin coupling constants

$J(^{13}C-^{1}H)$ for all groups of chemisorbed propene compared with gaseous propene was also observed. For hydrocarbons, a decrease in the value of the constant $J(^{13}C-^{1}H)$ reflects a decrease in the strength of the C–H bond.[106] A comparison of the experimental values of σ and $J(^{13}C-^{1}H)$ with the results of MINDO/3 calculations for different forms of adsorption was used to obtain the most probable model of the chemisorption of propene on $\gamma$-$Al_2O_3$.[105] According to this model, the propene molecules are bonded to the surface by interactions of two types: between the π-electrons of the double bond of propene and the surface Al atom, and between the protons of the methyl group and the surface O atoms.

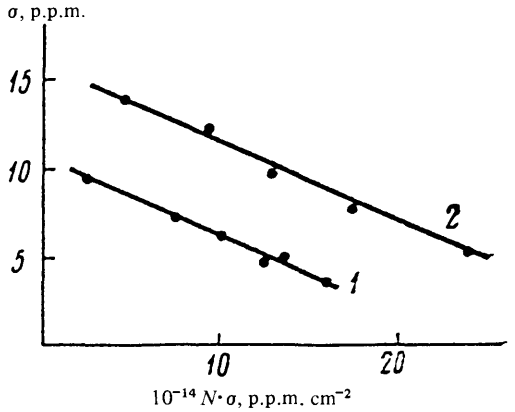



Figure 7. Plot of the chemical shift of propene adsorbed on $\gamma$-$Al_2O_3$ against $N.\sigma$ for different temperatures of treatment: *1*) 400 °C, *2*) 600 °C.[105]

Another example of the effective use of rotation at the magic angle to decrease the line widths for adsorbed molecules is provided by a study[107] of the $^{13}C$ NMR spectra of methane adsorbed on HZSM-5 zeolite. Rotation decreased the line widths considerably, making it possible to measure the change in not only the chemical shift but also the spin–spin coupling constant.[107] The signal from adsorbed methane is displaced to a weak field relative to methane in the gas phase. The spin–spin coupling constant decreases by ~10 Hz on adsorption. This indicates that a bond is formed between methane and surface centres, possibly leading to an increase in the length of the C–H bonds in the adsorbed molecule.

$^{13}C$ NMR with suppression of the spin–spin interaction with the protons has been used[108–110] to study the adsorption of ethylene enriched in the $^{13}C$ isotope on HZSM-5 zeolite at room temperature. The characteristic signal from ethylene (σ = 122 p.p.m.) was first observed. The intensity of this signal gradually decreased, and finally disappeared completely, indicating that ethylene is transformed into products which cannot be detected by NMR. The $^{13}C$ NMR spectra obtained with rotation of the specimens at the magic angle, immediately after the disappearance of the signal from ethylene, showed two lines at 28.8 p.p.m. and 13.5 p.p.m., assigned to aliphatic $CH_2$ and $CH_3$ groups respectively.[111] Both signals were broadened by dipole–dipole interaction between the carbon nuclei, but in spite of this, they showed a fine structure due to the presence of non-equivalent carbon atoms in the reaction products. Calculation of the relative intensity of the signals from the $CH_2$ and $CH_3$ groups[111] indicated that ethylene is converted into linear aliphatic hydrocarbons with 9–10 carbon atoms in the chain. The marked broadening of the lines and the fact that they cannot be observed without rotating the specimen at the magic angle indicate that the molecules of the reaction products form strong bonds with the zeolite.

$^{13}C$ NMR with rotation of the specimens at the magic angle and cross polarisation has also been used[112] to study the oligomerisation of alkenes on HZSM-5 zeolite. The chief products are linear oligomers at room temperature, and branched oligomers at high temperatures (~100 °C). This follows from a comparison of the values of σ with data for polymers with different structures. In contrast to this, on HY zeolites and H-mordenite, the alkenes are converted chiefly into branched oligomers at room temperature also. These differences are apparently due to the characteristic features of the structure of the HZSM zeolites, which have pores of smaller diameter.

## 4. The Study of the Adsorption on the Acidic Centres of Catalysts

Because of the important role of surface acidic centres in catalytic reactions, the adsorption of various molecules on these centres has been intensively studied for a long time by various physicochemical methods, mainly infrared spectroscopy.[113,114] Since $^{13}C$ NMR spectroscopy makes it possible to distinguish molecules in the free and adsorbed states, it has also been used to study surface acidic centres.[115–117]

The NMR spectra of a number of amines, including pyridine, aniline, and some of their derivatives, adsorbed on $SiO_2$, $Al_2O_3$, and an aluminosilicate, have been obtained.[115] On $SiO_2$, only a slight change in σ for the nuclei of the amines was observed, except for N,N-diethylaniline, for which an unusually large shift (–9 p.p.m.) of the signal of the C(4) carbon atom was observed; this may be due to a change in the geometry of the molecule on adsorption. The adsorption of amines on $Al_2O_3$ was accompanied by a much stronger interaction, but the spectra did not show the large chemical shifts usually observed when the corresponding amines are protonated in acidic solutions. This may be due to blocking of the strong acidic centres on the aluminium oxide surface. For the aluminosilicate, the values of σ were smaller than for the corresponding protonated amines in solution, and increased with decrease in the degree of covering of the surface. This last feature indicates that there is rapid exchange between the chemisorbed (protonated) and "free" (physically adsorbed) states of the amines. The rapid-exchange procedure was used[116] to study the adsorption of pyridine on silica gel treated with hydrochloric acid; the value of σ for chemisorbed pyridine was found to be close to the value for the pyridinium ion in aqueous solution.

In the simplest case, when there is exchange of an amine between two states, it is possible to write:[116]

$$\sigma = f_A\sigma_A + (1-f_A)\sigma_0 \qquad (7)$$

where σ is the observed chemical shift; $\sigma_0$ and $\sigma_A$ the chemical shifts for the free amine and for the amine combined with an acidic centre; and $f_A = N_A/N$ the proportion of amine molecules combined with acidic centres. If the amine can be combined with both Lewis and Bronsted acidic centres, generalisation of Eqn.(7) gives the expression

$$\sigma = f_H\sigma_H + f_L\sigma_L + (1-f_H-f_L)\sigma_0 \qquad (8)$$

where the subscripts "H" and "L" refer to Bronsted and Lewis centres respectively.

For the description of the dependence of $\sigma_H$ on the degree of covering of the surface in Ref.116 the value taken for $\sigma_H$ was that measured for the same amine in an acidic aqueous solution, the value taken for $\sigma_L$ was the value of the chemical shift for the complex of the amine with the Lewis acid $BF_3$, and the value taken for $\sigma_0$ was the value of the chemical shift for the amine adsorbed on $SiO_2$, which was assumed to have no surface acidic centres capable of protonating amines. Analysis (using Eqn.(8)) of the dependence of $\sigma$ on the degree of coverage for the adsorption of 4-ethylpyridine on the aluminosilicate showed good agreement between the values for the total number of acidic centres of the aluminosilicate obtained from the NMR spectra and from the adsorption of ammonia.

$^{13}C$ NMR has been used[118] to study the reaction of acetone with dehydroxylated and partly methylated silica gel specimens. An appreciable shift of the lines from the C=O group on the partly dehydroxylated specimens (by ~9 p.p.m. to a weak field) as a result of the formation of a hydrogen bond with OH groups was detected. The shifts for the methylated specimens were much smaller. The number of centres reacting with acetone was determined, and good agreement with the infrared spectroscopic data was obtained.

These studies were carried out using the standard high-resolution NMR procedure, which makes it possible to obtain well resolved spectra only when there is rapid movement of the adsorbed molecules on the surface. To obtain well resolved spectra for strongly adsorbed species, it is necessary to carry out the measurements at a fairly high temperature. This creates certain experimental difficulties, which can be overcome by using rotation of the specimens at the magic angle and cross polarisation to decrease the line widths. In Refs.119 and 120 these methods were used for the first time to study the adsorption of n-butylamine and pyridine on $\gamma$-$Al_2O_3$. The well resolved NMR spectra of n-butylamine showed the presence on the $\gamma$-$Al_2O_3$ surface of chemisorbed species of at least two types, due to the existence on the $\gamma$-$Al_2O_3$ surface of centres of two types interacting with the amine. Comparison with the spectra of the solid adducts of n-butylamine with HCl and $BCl_3$ made it possible to identify these centres as Bronsted and Lewis surface acidic centres. The separate observation of the lines from the amine adsorbed on these centres makes it possible in principle to use this method for the quantitative measurement of the numbers of acidic centres of different types.

The same procedure was used to study the spectra of pyridine adsorbed on $\gamma$-$Al_2O_3$. When the usual method of recording the spectra is used, pyridine gives broad poorly resolved lines even at increased temperatures and relatively high degrees of coverage. The use of rotation of the specimen at the magic angle combined with cross polarisation makes it possible to observe for pyridine adsorbed on $\gamma$-$Al_2O_3$ a completely resolved spectrum for all three non-equivalent carbon atoms. The values of $\sigma$ coincide with the corresponding values for liquid pyridine, indicating that the adsorbed pyridine molecules are weakly bound to the surface. When cross polarisation was used, lines of anomalous intensity were observed, and this can be attributed to the characteristic features of the dynamics of cross polarisation when the movement of the pyridine molecules in the adsorbed state is anisotropic. The results of the experiments agree with a model in which the pyridine molecule reacts with the surface via the nitrogen atom and rotates chiefly about the $C_2$ axis.

Extensive possibilities for the investigation of acidic centres are opened up by the study of the $^{15}N$ NMR spectra of adsorbed bases. Although the $^{13}C$ NMR spectra can be obtained at the natural concentration of the isotope, however, the much lower intensity of the signal from $^{15}N$ nuclei makes it necessary to use enriched specimens. The study of the $^{15}N$ NMR spectra of adsorbed bases is of particular interest, since both the protonation of these substances and their formation of a hydrogen bond with surface OH groups often take place directly via the nitrogen atom. As a result, the differences in the chemical shifts of the $^{15}N$ signals for the protonated and non-protonated molecules are greater than those for $^{13}C$ and $^{1}H$ nuclei. Few papers have yet been published, however, on the use of $^{15}N$ NMR to characterise surface acidic centres.

The $^{15}N$ NMR spectra of ammonia, trimethylamine, pyridine, and acetonitrile adsorbed on zeolites have been studied.[121] The spectra of pyridine on Y zeolite showed shifts (of ~90 p.p.m.) relative to the signal of pyridine adsorbed on $SiO_2$, indicating that pyridinium ions are formed. The number of OH groups interacting with pyridine was determined. The unusually large shifts obtained for a number of specimens were attributed to the formation of complexes with Lewis acid centres on the surface.

When pyridine was adsorbed on modified silica gels, the values of $\sigma$ in the $^{13}C$ NMR spectra remained practically unchanged, whereas the $^{15}N$ NMR spectra showed shifts of ~20 p.p.m. as a result of the formation of a hydrogen bond between pyridine and the OH groups of silica gel.[122] In the case of silica gel modified with phosphorus, the formation of pyridinium ions was observed, apparently as a result of the reaction with P–OH groups.

In a study of the $^{13}C$ and $^{15}N$ NMR spectra of acetonitrile adsorbed on zeolites containing $Li^+$, $Na^+$, $Rb^+$, $Cs^+$, and $Ag^+$ cations,[123] it was found that the exchange cations act as adsorption centres, leading to shifts of the signals in the $^{15}N$ NMR spectra. The $^{13}C$ and $^{15}N$ NMR spectra of pyridine adsorbed on an aluminosilicate have been studied[124] using cross polarisation and rotation at the magic angle. The reaction of pyridine with the surface centres of the aluminosilicate leads to a decrease in the difference in the chemical shifts in the $^{13}C$ NMR spectra for the $\alpha$- and $\beta$- and for the $\alpha$- and $\gamma$-carbon atoms of pyridine. Comparison of these values with the corresponding values for pyridine forming a hydrogen bond (a solution of pyridine in water) and for pyridine forming a coordinate bond with aluminium (the compound $C_5H_5NAl(C_2H_5)_3$) indicated that at low degrees of covering, pyridine is adsorbed chiefly on Lewis centres; the comparison also made it possible to calculate the proportion of pyridine combined with these centres, and to determine their absolute concentration. At high degrees of covering, most of the pyridine molecules form hydrogen bonds with OH groups.

An analysis of the $^{15}N$ NMR line widths indicated that there is movement of the adsorbed pyridine molecules on the surface.[124] Experiments on cross polarisation of the $^{13}C$ nuclei with different times of thermal contact between the spin systems showed that this movement is anisotropic. It apparently involves rotation of the pyridine molecule about the two-fold axis.

### 5. The Study of the Adsorption of Hydrogen

NMR is convenient for the study of adsorbed hydrogen, since it is highly sensitive to the electronic state and mobility of the adsorbed molecule. A large number of studies have been carried out by broad-line NMR or by nuclear magnetic relaxation to determine the correlation time of the movement of the molecules on the catalyst surface; these studies have been reviewed.[2,3] Recently, as a result of the development of spectrometers operating with high fields, it has become

possible to use NMR spectroscopy to measure the chemical shifts of adsorbed hydrogen.

A study of the spectra of hydrogen adsorbed on an $Rh/TiO_2$ catalyst detected two forms of hydrogen.[125] For the first, the value of $\sigma$ was close to that for TMS; this hydrogen is bound to rhodium. The second form of hydrogen has a very high mobility; this hydrogen reacts for a short time with surface paramagnetic $Ti^{3+}$ ions, leading to a strong-field shift of the signal. The mobile form is possibly produced by the dissociation of hydrogen molecules on rhodium with subsequent transfer of active hydrogen to the catalyst surface. After the combined adsorption of CO and $H_2$, the signal from the mobile hydrogen disappears, and the total absorption of hydrogen by the catalyst increases as a result of the formation of new species containing protons.[126]

A study of the $^1H$ NMR spectra of reduced copper–chromium catalysts for the partial hydrogenation of unsaturated hydrocarbons[127,128] indicated that the structure of the reduced catalysts contains an atomic form of hydrogen which brings about the selective hydrogenation of the hydrocarbons. The hydrogen species in these catalysts, which have the spinel structure, are situated close to the paramagnetic ions and have a low mobility, leading to marked broadening of their lines.

The adsorption of hydrogen on platinum has been studied.[129] Hydrogen may be present on platinum in two states: strongly (irreversibly) bound and weakly (reversibly) bound. On the basis of the first results, obtained in Ref.130 at high hydrogen pressures, it was possible in Ref.129 to detect two signals for platinum deposited on silica gel. The high-field signal with $\sigma \cong -50$ p.p.m. is due to irreversibly adsorbed hydrogen. This high value of $\sigma$ indicates a strong interaction between hydrogen and platinum. It is suggested that the atoms of this form of hydrogen are situated in the interstices of the surface platinum species. The signal close to that of TMS was assigned to hydrogen reversibly adsorbed on isolated platinum atoms.

A more detailed study[131] showed that for pure monodisperse platinum specimens deposited on $SiO_2$, the spectrum shows only the high-field signal, and the signal close to that of TMS is due to the presence of impurities in the specimens. It was also found that hydrogen in the presence of deposited platinum influences the spin–lattice relaxation of the Si–OH groups of the carrier. This effect is not observed for $SiO_2$ without platinum. It was suggested that the rate of the relaxation of the OH groups is increased by paramagnetic hydrogen atoms "flowing" from the platinum to the carrier. Further studies are required, however, for a more reliable explanation of the reasons for this effect.

Large strong-field shifts of the hydrogen signal, apparently due to the formation of hydride-like structures, have also been observed for other metals of the platinum group: Ru, Rh, Pd, Os, and Ir.[132] In the case of palladium, an averaged signal from chemisorbed hydrogen and hydrogen dissolved in palladium was observed. In the case of Ru and Os, the chemical shift for hydrogen was independent of the covering, but in the case of Rh it even increased with increase in the degree of covering of the surface by hydrogen. These effects have not yet been satisfactorily explained.

The adsorption of hydrogen on $Rh/Al_2O_3$ has been studied.[133] The $^1H$ NMR spectrum obtained consists of three lines: a line with $\sigma = -(10-15)$ p.p.m. from a surface hydride, a Pake doublet with a splitting of ~44 kHz from water molecules formed during the adsorption of hydrogen, and a narrow line from physically adsorbed hydrogen. Analysis of the spectrum shows that on the $Rh/La_2O_3$ catalyst, the activation of hydrogen involves hydride formation. The subsequent "flow" of activated hydrogen to the carrier may lead to partial reduction of the carrier surface. The water molecules formed in this process are firmly bound to metallic rhodium. Thus NMR spectroscopy makes it possible to observe the activation of hydrogen on metallic rhodium and its subsequent migration to the carrier.

The spectra of hydrogen adsorbed on $\gamma$-$Al_2O_3$ have been studied.[134] A single line was observed, due to rapid exchange between different forms of adsorbed hydrogen.

In a study of the adsorption of hydrogen on zinc oxide,[135] it was suggested that on the surface there is a weakly bound form $H_3^+$, produced by the reaction of hydrogen with a hydroxide group. This suggestion was based on the fact that the $^1H$ NMR spectrum showed a weak line with $\sigma \cong 15$ p.p.m. from the overall spectrum of the OH groups and physically adsorbed hydrogen; it requires verification.

While the present review was being prepared for publication, additional data appeared on the study of the local environment of silicon from the $^{29}Si$ NMR spectra[136–147] and the study of the acidic properties of the surface from the $^{31}P$ NMR spectra of phosphorus containing bases in HY zeolites.[148] High-resolution proton magnetic resonance has been used[149–151] to study the Bronsted acidic centres of amorphous aluminosilicates and zeolites. The high-resolution $^{17}O$ NMR spectra of solid oxides and zeolites have been studied.[152,153] Hydrocarbon complexes on catalyst surfaces have been studied.[154,155] There has recently been considerable interest in the high-resolution $^{27}Al$ and $^{31}P$ NMR study of aluminium phosphate catalysts with zeolitic structures.[156,157] Studies of heterogeneous catalysts and the processes taking place on their surfaces, carried out in the Soviet Union using the methods of the high-resolution NMR spectroscopy of solids, have been reviewed.[158]

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The data given in the present review show that the production of a new generation of highly sensitive multi-nuclei NMR spectrometers and the development of various procedures for obtaining high-resolution NMR spectra for solid specimens have led to qualitative changes in the possibilities provided by NMR for the study of heterogeneous catalysis. This method can be used to carry out systematic studies of catalyst structures, the forms of adsorption of reagents, and their transformations in catalytic reactions.

The important role in the development of organic and inorganic chemistry, including homogeneous organic and metal-complex catalysis, now being played by the study of substances and processes in solution by the traditional method of high-resolution NMR is well known. The data presented in the present review indicate that in the near future, modern versions of the NMR method will begin to play a similar role in the development of heterogeneous catalysis.

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# The Study of Heterogeneous Catalysts by the EXAFS Method

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The principles of the EXAFS method, which makes it possible to determine the structure of the local environment of a chemical element being studied within a radius of 4 Å, are described. Information on the experimental apparatus, the fields of application, and the accuracy of the determination of the structural parameters (interatomic distances, coordination numbers, Debye-Waller factors) are given. Examples of the use of the method to study catalysts are described.
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## I. INTRODUCTION

In the last ten years, a fundamentally new method has been developed for determining the local structure of the environment of a given chemical element in any state of aggregation, namely the EXAFS method. (EXAFS is an abbreviation for Extended X-Ray Absorption Fine Structure, or DTSRSP in Russian). Unlike traditional diffraction methods, which make use of the phenomenon of the elastic scattering of the probing radiation (X-rays, electrons, neutrons) on a crystal lattice, the EXAFS method makes use of the characteristic absorption of X-rays by the chemical element being studied, which is independent of the existence of a crystal lattice. Thus the EXAFS method can be used to study materials amorphous towards X-rays, such as, for example, highly dispersed deposited catalysts. The present review describes the principles of the EXAFS method and describes its possible applications in the study of catalysts.

## II. PRINCIPLES OF THE METHOD

In X-ray absorption spectroscopy, use is made of processes involving the transfer of an electron from an inner level, usually 1*s*, 2*s*, and 2*p*, to higher unoccupied levels or to the free state, that is ionisation. Fig.1 shows the hypothetical X-ray absorption spectrum of an isolated atom. When the X-ray quantum reaches an energy $E_0$ sufficient to ionise the electrons of one of the inner levels, a sudden jump is observed. Before this point, absorption involves higher-lying levels and is described by an expression of the form $A.E^{-3} + B.E^{-4}$ (where $E$ is the energy of the X-ray quantum, and $A$ and $B$ are parameters specific for each chemical element). When the energies of the quanta are greater than the ionisation potential of this level, a regular decrease in the absorption coefficient according to the same law should be observed.

For a real specimen, where there are other atoms in the local environment of the absorbing atom, the absorption spectrum has a different appearance. Fig.2 gives the X-ray absorption spectrum of metallic platinum with ionisation of the $2p_{3/2}$ level; the spectrum shows a complex structure close to the absorption edge and oscillation over a very wide range, from 50 eV to ~1000 eV. These oscillations have been called the extended X-ray absorption fine structure.

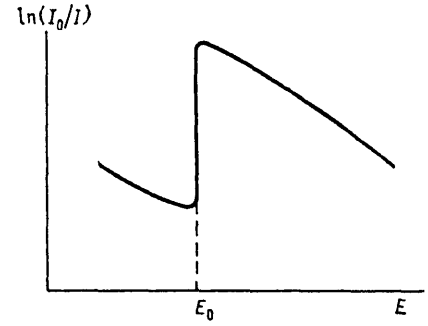



Figure 1. Assumed X-ray spectrum of an isolated atom: $I_0$ is the intensity of the incident radiation, $I$ the intensity of the radiation passed through the specimen, $E$ the energy of the X-ray quantum, and $E_0$ the ionisation potential of one of the inner levels of the atom.

The phenomenon was discovered[1] in the nineteen-thirties. In the nineteen-fifties, the following model was developed[2,3] to explain the nature of the phenomenon; for an isolated atom, a photoelectron ejected by an X-ray quantum is described by a spherically symmetrical divergent wave-function. When there are other atoms close to the absorbing atom, the photoelectron will be partly scattered backward

on these atoms, and its state will be described by the superposition of the emitted and scattered wavefunctions. This leads to a change in the absorption coefficient. The absorption coefficient will increase or decrease, depending on the phase in which the wave front of the scattered photoelectron returns to the absorbing atom. If the wavelength of the ejected photoelectron is changed by changing the energy of the incident quantum, sinusoidal fluctuations will be observed in the absorption spectrum, with a period equal to twice the distance between the absorbing and scattering atoms.

The total spectrum will contain oscillations of this kind from all surrounding atoms. By determining the period of the oscillations in the absorption spectrum, it is possible in principle to measure the distance from the absorbing atom to the scattering atom, and, by determining the amplitude of the oscillations, to measure the number of scattering atoms. The determination of interatomic distances by this method has an important advantage, since it is possible to measure the distances around the atom of one chemical element. The atoms of other chemical elements, which are present, for example, in multicomponent systems such as catalysts, do not interfere in these measurements, since as a result of the large energy range over which the absorption edges of the inner levels of the atoms of different chemical elements are distributed, the superposition of the absorption edges of different elements is fairly infrequent.

The first attempts to determine interatomic distances by this method were unsuccessful,[4] however, because in the emission and scattering of photoelectrons, additional displacements of the phase of their wavefunction may occur, and it became possible to calculate these displacements, and also the amplitudes of the probability of the scattering process, only in the mid nineteen-seventies.

With the development of computing techniques, the model was refined, the forms of the interatomic potentials were selected, and numerical calculations were carried out to determine the amplitudes of the probability of the scattering of the photoelectron and the magnitude of the phase displacements in the emission and scattering of the photoelectron.[5-9] Experimental verification showed that the model chosen for the phenomenon is correct, and confirmed that the accuracy attained in the calculations and the fact that the phase displacements are independent of the chemical state of the scattering and absorbing atoms make it possible to determine interatomic distances by means of a Fourier analysis of the fine structure of the X-ray absorption spectrum.[10] The limitations of the model lead mainly to uncertainty in the determination of the coordination numbers and the amplitudes of the thermal vibrations of the atoms, and have little influence on the accuracy of the determination of interatomic distances. Nevertheless, the complexity of the experiment (the recording of a single spectrum on a laboratory instrument even at the present time can take days) would have prevented EXAFS spectroscopy from developing into an analytical method if the synchrotron emission from electron storage rings had not begun to be more widely used in X-ray spectral studies.

## III. APPARATUS AND FIELDS OF APPLICATION

Synchroton emission (SE) is the emission by relativistic electrons in their movement along the annular orbit of the storage ring. The spectral range of SE extends from the infrared to the X-ray region. The intensity of SE is hundreds of times that of the emission of the resonance lines of the X-ray tubes usually employed for structural analysis; SE is continuous throughout its spectral range. This makes it possible to carry out experiments over a wide range of energies, to change easily from one element to another, and to work with lower concentrations of absorbing elements. Moreover, the SE beam has a very low angle of divergence ($10^{-3}$ rad) and a high degree of polarisation.[11,12]

Because of these advantages of SE, and in spite of the need to construct special apparatus, an increasing proportion of X-ray spectral studies are being carried out using it. The first studies were carried out in parallel with experiments on high-energy physics, but many countries, such as the USA, Britain, France, West Germany, Italy, and Japan, now have electron storage rings that are used only to generate SE as

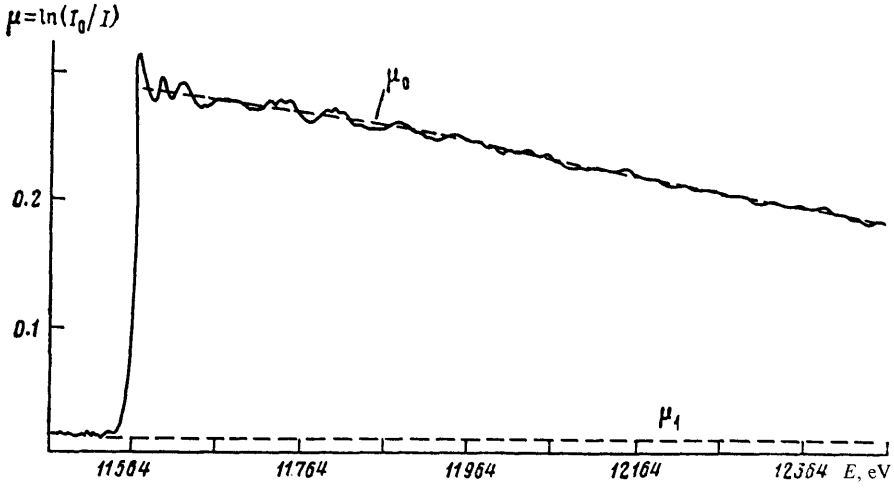



Figure 2. X-Ray absorption spectrum of the $L_{III}$ level of metallic platinum: $\mu$ is the absorption coefficient, $\mu_0$ the smooth part of the absorption coefficient, and $\mu_1$ the absorption of other electron levels in the atom.

a source for X-ray studies. The use of SE for EXAFS spectroscopy has made it possible to decrease the time taken to record the spectrum from days to 10–20 minutes and to work at concentrations of the element being studied reaching 0.1 M in a weakly absorbing matrix.

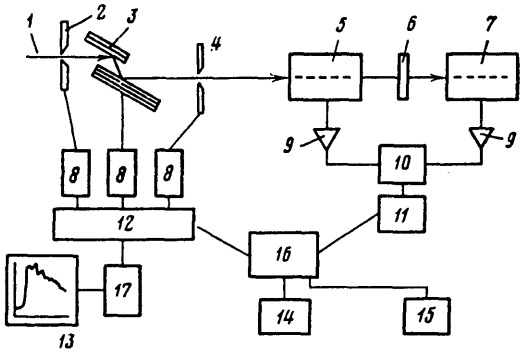



**Figure 3.** Block diagram of an EXAFS spectrometer: *1*) beam of synchrotron radiation, *2*) inlet slit of the monochromator, *3*) single-block crystal double monochromator, *4*) outlet slit of the monochromator, *5*) flow-through ionisation chamber, *6*) specimen, *7*) total absorption ionisation chamber, *8*) stepped motor control blocks, *9*) pre-amplifier, *10*) commutator, *11*) digital voltmeters, *12*) KAMAK box, *13*) display, *14*) video terminal, *15*) digital printer, *16*) ODRA-1305 computer, *17*) display control block.

In the USSR, EXAFS spectroscopic studies are being carried out using the electron storage rings of the Institute of Nuclear Physics of the Siberian Branch of the Academy of Sciences of the USSR in the Siberian Collective Centre for the Use of Synchrotron Emission. An EXAFS spectrometer (Fig.3) has been constructed for this purpose, and is in regular operation.[13] A general description of the principles of the construction of spectrometers for use with SE can be found in Ref.12. It should be noted only that when the generally employed two-crystal monochromator scheme (with Ge(111) and Si(220) crystal monochromators) is used to record the spectrum, no change takes place in the direction of the propagation of the X-ray beam after passing through the monochromator. Only a lateral displacement of the X-ray beam takes place, leading to a displacement of the beam along the specimen when the spectrum is recorded (by ~0.02 mm).

The recording system should ensure the measurement of the intensity of the quantum flux with an uncertainty of not more than $10^{-4}$ and the measurement of the absorption coefficient with an uncertainty of not more than 0.1% for an intensity of the incident radiation of $10^{13}$ photon $rad^{-1}\,s^{-1}$ with $\Delta\lambda/\lambda \cong 3 \times 10^{-4}$.

EXAFS spectrometers of different types have now been developed. They differ in the construction of the monochromator system and mainly in the recording system. Changes in the monochromator system are made to give a "purer" signal at the outlet by decreasing the scattered background and the contribution from higher harmonics. The choice of the method of recording the spectrum depends on the problem being studied. A whole set of procedures has now been developed. The most widely encountered scheme for operating the instrument "in transmission" makes it possible to record the EXAFS spectra from an element in a matrix whose absorption is slight compared with that by the element being studied in the range of quanta energies used, for example the spectra of $Pt/SiO_2$ and $Pd/TiO_2$ catalysts. The concentration of the element being studied may reach 1 mass %.

When the absorption by the matrix is strong compared with that of the element being studied close to its ionisation potential ($Ti/SiO_2$, $Pt/TiO_2$), the EXAFS spectra cannot be obtained by this method, since the strong absorption by the carrier leads to a decrease in the accuracy of the measurement of the absorption coefficient. For the study of these materials or for the study of surfaces, other methods are employed, which make use of the fact that the primary process in the absorption of X-rays is accompanied by secondary processes of X-ray and optical fluorescence or the emission of Auger electrons. The system of recording X-ray fluorescence[14] makes it possible to increase the sensitivity with respect to the element being studied by factors of 10–100 and to work with strongly absorbing matrices.

The recording of Auger electrons,[15,16] the total electron photocurrent,[17,18] or the X-ray-induced desorption of ions[19] makes it possible to study the structure of a surface and the coordination of molecules adsorbed on a surface. The thickness of the surface layer that can be studied reaches 100 Å for the total-photocurrent method, and 2–10 Å for methods using the recording of Auger electrons or the X-ray-induced desorption of ions.

Other methods are now being developed, which make it possible to study the structure of the surface of a catalyst not in a vacuum but in the presence of a reaction medium (the total external reflectance method[20]) or to carry out a selective study of the structure of the environment of the atoms of an element in states which luminesce in the optical range of the spectrum under the influence of X-rays.[21]

## IV. METHODS OF EXTRACTING STRUCTURAL DATA

In the model described above, the extended X-ray absorption fine structure is described by the function[10]

$$\chi(k) = \frac{1}{k}\sum_i \frac{N_i}{R_i^2} f_i(k)\, e^{-\sigma_i^2 k^2} e^{-R_i/\lambda} \sin(2kR_i + \varphi_i(k)) \qquad (1)$$

where $k$ is the modulus of the wave vector of the photoelectron, $k = [2m_e \times (E_0 - E)/\hbar^2]^{1/2}$, $E_0$ the ionisation potential of the absorbing electron level, $N_i$ the number of atoms in the $i^{th}$ coordination sphere, $R_i$ the radius of the $i^{th}$ sphere, $\sigma_i^2$ the Debye–Waller factor, $\lambda$ the free path of the photoelectron, $f_i(k)$ the amplitude of the probability of the scattering "backward" and $\phi_i(k)$ the change in phase during emission and scattering. The summation is carried out over all coordination spheres.

$\chi(k)$ is determined from the experimentally measured absorption spectrum using the equation

$$\chi(k) = (\mu - \mu_0)/(\mu_0 - \mu_1)$$

where $\mu$ is the absorption coefficient of the atom being studied in the specimen, $\mu_0$ the absorption coefficient of the same atom in the isolated state, and $\mu_1$ the absorption coefficient of the atoms of other elements present in the specimen, and of other levels of the atom being studied (see Fig.2).

There are several methods for analysing $\chi(k)$. The simplest is the Fourier transformation of $\chi(k)$, which gives a series of maxima displaced relative to the origin of coordinates by an amount $2R_i + \delta_i$, where $\delta_i$ is the linear part of

$\phi_i(k)$.[10] If the summation with respect to $i$ in Eqn.(1) is replaced by integration with respect to the distribution function $\rho(R)$,[22] it is possible to find a direct solution of the integral equation obtained. In addition, extensive use is made of modelling, where the parameters to be determined are varied to give best agreement between the experimental and model spectra.[23]

All these methods have advantages and disadvantages, and preference cannot yet be given to any one of them. The direct solution of the integral equation is possible only for one-component systems, and the results depend markedly on the uncertainty in the determination of the experimental data. This method therefore finds only limited application, and is unsuitable for the study of catalysts.

The methods of Fourier analysis and modelling are most widely used. Fourier analysis is applicable to all systems, does not require the introduction of additional assumptions, and gives reliable information. Its main unsatisfactory feature is that the analysis is carried out over a limited range of wavenumbers, 12–15 Å$^{-1}$. The narrowness of the range leads to a large apparatus width in the Fourier transformation for the atom radial distribution function being sought, and this makes it difficult to analyse complex systems, because of the overlap of the peaks. The necessary restriction of the range of integration at low wavenumbers to 3–4 Å$^{-1}$, below which the photo-ionisation model used is inapplicable, leads to the appearance of additional interference distortion on the atom radial distribution curve, as a result of which additional splitting and displacement of the peaks are possible. Moreover, Fourier analysis does not make it possible to determine the nature of the scattering atoms, and it is necessary to seek a correction for the phase displacement $\delta_i$, by making assumptions about the nature of the scattering element on the basis of additional information about the material being studied.

In the modelling method, the nature of the scattering atom and, usually, the functions $f_i(k)$ and $\phi_i(k)$ for this atom are given. The experimental spectrum and the Fourier filtration procedure are then used to separate the oscillations corresponding to the distance being analysed. The parameters $R_i$, $N_i$, $\sigma_i^2$, $E_0$, and, in individual cases, $\lambda$ are varied. This method gives a higher accuracy of the determination of the interatomic distances, compared with Fourier analysis, and makes it possible to find the atomic number of the element to within ±5. The parameters being varied are correlated ($E_0$ and $R_i$, $N_i$ and $\sigma_i^2$), however, because of the internal characteristics of the approximation used and the narrowness of the wavenumber range for which it is possible to obtain experimental data. The existence of this correlation may lead to errors in the determination of the parameters. The most reliable results are therefore obtained by a combination of both methods, where the primary analysis is carried out by the Fourier method, after which the results obtained are refined by modelling.

Fig.4 gives the results of a Fourier analysis of the function $\chi(k)$ for the absorption spectrum of the $L_{III}$ level ($2p_{3/2}$ level) of metallic platinum, given in Fig.2. Fig.4 shows that, in accordance with Eqn.(1) with increase in $R$ the intensity of the peaks decreases rapidly (as $R^2$). This feature, and also the damping of the function $\chi(k)$ as a result of the loss of energy by the photoelectrons with long free paths in inelastic scattering processes, restricts the range of interatomic distances that can be measured to 1.5–4.0 Å. The lower limit is determined by the need to have several oscillation periods on the experimental curve. The positions of the peaks in Fig.2 also do not correspond to the true distances between the atoms in metallic platinum. This difference is determined by the change in phase $\phi(k)$. Special studies have shown[24,25] that the observed displacement $\delta_i$ depends only on the nature of the absorbing and scattering elements, and not on their chemical state. The fact that $\phi_i(k)$ is independent of the chemical state makes it possible to determine interatomic distances with a high accuracy (from 0.04 Å to 0.01 Å for different methods). Tables of functions $f_i(k)$ and $\phi_i(k)$ for the ionisation of the $K$ and $L$ levels have now been published[9] for practically all chemical elements.

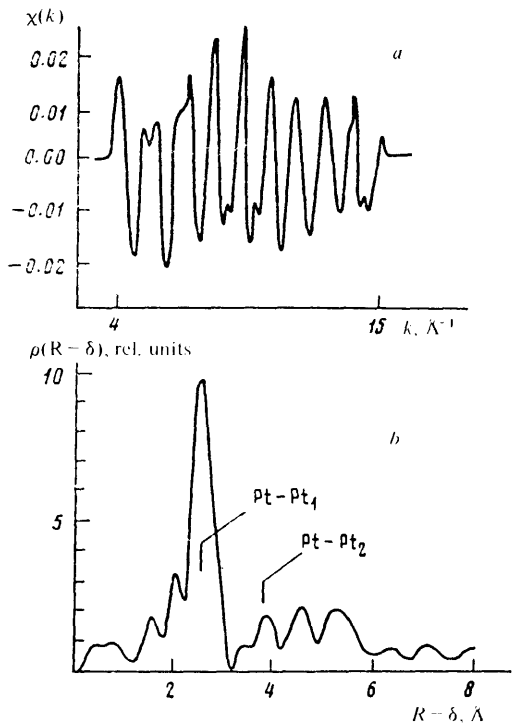



**Figure 4.** Extended X-ray absorption fine structure of the $L_{III}$ level of metallic platinum (*a*) and the radial distribution function of the atoms obtained from it (*b*).

The accuracy of the determination of coordination numbers is much lower than that for distances. There are several reasons for this. Firstly, the amplitude of a peak on the experimental curve is determined by the integral magnitude of $f_i(k)$ in the range in which the experimental data are analysed. A large contribution to the amplitude is therefore made by the scattering of low-energy photoelectrons, and the amplitude for a given coordination number depends markedly on the chemical state of the scattering atom.[25,26] Secondly, all the effects which are present in photo-ionisation and scattering processes and which are not taken into account in the model used also influence primarily the amplitudes of the peaks. Processes such as inelastic scattering give a value of the coordination number being determined which is too low,[27] whereas multiple scattering may give a value of the coordination number which is too low or too high[28] and may even lead to the appearance of spurious peaks.[29] At the present time it is considered that the EXAFS method can be

used to determine coordination numbers of the first coordination sphere to within 20%; for subsequent spheres the uncertainty may reach 100%.[23]

A systematic analysis of the accuracy of the determination of the Debye–Waller factor by the EXAFS method has not been carried out, although the method is used for this purpose.[23] It has been shown that the possibility of using the EXAFS method to determine interatomic distances and coordination numbers depends markedly on the magnitude of $\sigma_i^2$.[30] For values of $\sigma_i^2 > 0.04$ Å$^2$, oscillations are not observed in the EXAFS spectrum. In some cases this leads to a situation in which any changes in the environment of the ligand atom being studied are not reflected in the spectrum.[31]

The treatment of the spectra is now being carried out everywhere by practically identical methods using similar computer programs. Work is being carried out to extend the possibilities provided by the programs. Thus an attempt has been made,[28,29] by estimating the influence of double scattering on the amplitude of the peaks in the EXAFS spectrum, to determine the angular distribution of the atoms in the second and higher coordination spheres.

## V. APPLICATIONS IN THE STUDY OF CATALYSTS

The number of publications devoted to the study of catalysts by the EXAFS method has now reached several hundreds. The first reviews of these studies have been published.[23,32] The present section will examine mainly studies of deposited metallic catalysts, which make up a large proportion of the work carried out. This is related both to their extensive practical application and to their relative simplicity. These catalysts are distinguished by the ease of selecting model compounds, for which metals are used. In view of the practical importance of deposited platinum catalysts, most studies deal with these materials. Most studies have dealt with the effect on the structure of small metal particles of the adsorption of various molecules and of the interaction of the deposited metal with the support.

For platinum particles with dimensions of 20 Å or less, a significant change in the radius of the first coordinations sphere, normally a decrease, has been observed. The effect is observed on different supports, such as $SiO_2$, $Al_2O_3$, and HY zeolite.[33–36] The decrease in the metal–metal interatomic distances compared with metal foil reaches 0.2 Å. The reason for this effect is not yet clear. It is suggested that it is due to a change in the electron density in the metal as a result of surface effects, for example chemisorption. In contrast to this, in a study[37] of the dependence of the structure of platinum deposited on $\gamma$-$Al_2O_3$ on its degree of dispersion, an increase in the length of the Pt–Pt bond by 0.14 Å compared with platinum foil was observed in the most highly dispersed particles reduced at 470 K (see Fig.5). Estimation of the coordination numbers by comparing the intensities of the peaks in the catalyst and in Pt foil made it possible to establish with an uncertainty of 20% that the coordination number for the Pt–Pt distance is 3. This indicated that in this system, nuclei of metallic clusters are produced in the form of tetrahedra of platinum ions, stabilised in aluminium atom vacancies in the $\gamma$-$Al_2O_3$ lattice.

It should be noted, however, that the coordination number determined by the EXAFS method is averaged over all atoms of the element being studied. It is not excluded, therefore, that some of the platinum atoms are in the monoatomic form (coordination number for the Pt–Pt distance equal to zero), while the rest are present as large particles (coordination number 9–12). This apparently explains the fact that increasing the temperature of treatment to 670 K leads to the appearance of particles in which the Pt–Pt distance is the same as in the massive metal, while the coordination number is very small and equal to 3 (Fig.5*b*).

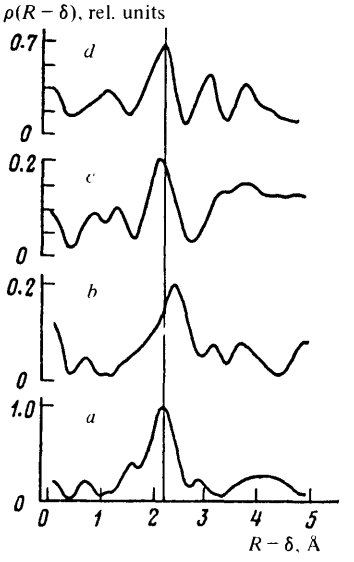



Figure 5. Radial distribution function of the atoms of metallic platinum (*a*) and catalysts with the composition 2.5 mass % $Pt/Al_2O_3$, reduced at 470 (*b*), 670 (*c*), and 870 (*d*) K.

A number of authors have studied the influence of the adsorption of various gases on the structure of the platinum particles. The adsorption of oxygen on highly dispersed catalysts at room temperature leads to a decrease in the Pt–Pt distance.[34–36] For catalysts deposited on $\gamma$-$Al_2O_3$ (particle size ~20 Å)[36] and on HY zeolite (particles 12 Å),[35] the decrease is 0.2 Å, and for catalysts deposited on $SiO_2$ (20 Å) it is 0.12 Å.[34] The adsorption of hydrogen leads to an increase in the length of the Pt–Pt bond to the value characteristic of the massive metal.[34] The adsorption of CO does not lead to a change in the interatomic distances.[35]

The possibility of following the phase composition of deposited catalysts by the EXAFS method has been demonstrated for deposited platinum catalysts treated with oxygen at high temperatures. In addition to metallic platinum, the phases PtO,[36] $\beta$-$PtO_2$,[38,39] and $Pt_3O_4$ [40] were observed. The change in the ratio of the intensities of the peaks corresponding to the Pt–O distances in the oxide and the Pt–Pt distances in the metal was used to determine the dependence of the ratio between the phases on the method of treatment of the specimen. Reaction with oxygen gives a range of oxides whose structure is perturbed by the interaction with the carrier, and which are very difficult to reduce.

The advantages of the EXAFS method are most clearly revealed in the study of multicomponent catalysts, if it is possible to study separately the environment of the atoms of each of the chemical elements making up the active fraction of the catalyst. An analysis of the environment of the Pt and Re atoms in platinum–rhenium reforming catalysts has been carried out.[41] The study of the absorption spectra of the $L_{III}$ level of the rhenium atoms established that when

platinum is deposited on rhenium catalysts obtained by reducing $[Re(OC_2H_5)_3]_3$ with hydrogen at 870 K, the platinum (at ratios Pt/Re = 1/3 and 2/3) is adsorbed on $Re_3^{n+}$ trimers, reoxidizing them. This is revealed by a decrease in the Re–Re distance. On subsequent reduction of Pt, the Re–Re distance increases, but comparison of the EXAFS spectra for Re and Pt indicates that the length of the Re–Pt bond remains unchanged and that platinum is stabilised not on $SiO_2$ but on rhenium ions. This effect is not observed with an excess of platinum relative to rhenium.[42]

Among non-metal systems, the EXAFS method has begun to be used to study oxide[32] and sulphide W and Mo hydrodesulphurization catalysts.[43,44] When W and Mo are deposited on $SiO_2$ and then treated with sulphur, surface oxide sulphides are formed, leading to a marked change in the nature of the metal–metal bond.[44] The metal ions are separated into pairs, within which the distance between the atoms is shorter than in tungsten and molybdenum disulphides, and the pairs themselves are separated from one another by larger distances. The position of the promoter (nickel) in W–Ni catalysts relative to the atom of the main element, which forms W–S–Ni bonds, has also been determined.

Thus the EXAFS method has now passed through the stage of methodological development, and is beginning to produce its first results. Its further application, particularly in the study of catalyst surfaces, will undoubtedly provide fundamentally new information.

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# Application of Electron Paramagnetic Resonance and Ultraviolet Spectroscopy to the Study of Coordination-unsaturated Transition Metal Ions on the Surfaces of Catalysts

V.A.Shvets

The methodological characteristics of the application of the EPR and ultraviolet spectroscopic methods to the study of heterogeneous catalysts and reactions on their surfaces are briefly described. The concept of the coordination-unsaturated ions and the causes hindering their identification on catalyst surfaces by spectroscopic methods are discussed. Studies where the coordination and valence states of the surface coordination-unsaturated transition metal ions and their properties have been investigated with the aid of EPR and diffuse scattered light ultraviolet spectroscopy are examined. Data concerning the formation of surface complexes by the coordination-unsaturated ions with adsorbed molecules are analysed.
The bibliography includes 190 references.

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## INTRODUCTION

The electron paramagnetic resonance (EPR) and ultraviolet and visible spectroscopic methods have come to be widely used in chemistry because of the large amount of information which they can yield. They have been widely employed also in heterogeneous catalysis for the investigation of the structures and properties of catalysts, adsorption, and reaction mechanisms. The majority of heterogeneous catalysts are known to contain transition metal ions and such catalysts will be in fact be considered in this review.

The ideas of the chemistry of coordination compounds and of the ligand and crystal field theories, according to which the central ion of the complex or the transition metal ion of the catalyst are in an electric field generated by the ligands in their immediate vicinity, proved applicable to the description of the structures of the surfaces of heterogeneous catalysts, the properties of the transition metal ions in their composition, and the nature of the surface compounds. Within the framework of these theories, it is possible to describe fairly adequately the dependence of the optical and EPR spectra of the transition metal ions in the catalysts on the symmetry of the first coordination sphere and on the nature of the chemical bonds between the ion and the ligand. This leads to the possibility of determining from spectroscopic data the electronic and geometrical structures of the active centres of the catalysts containing transition metal ions and the changes undergone by them following the adsorption of various molecules.

The so-called coordination-unsaturated (CU) ions are considered in the majority of investigations as the active centres of the catalysts containing transition metal ions. The concept of the existence of CU ions follows naturally from the development of our knowledge of the structures of the lattices of solids and conditions in their activation necessary for the appearance of catalytic activity. In fact, heterogeneous catalysts become active as a rule after treatment at fairly high temperatures, i.e. under conditions where the surface hydroxy-groups and adsorbed water molecules are at least partly removed. It might have been supposed that vacant sites appear as a result of these processes in the coordination spheres of the surface cations. This concept is so natural that it led to a wide-scale employment of the concept of CU ions in heterogeneous catalysis.[1-4] However, the study of the electronic structures of these ions and of their coordination and valence states (the term valence state is used in this review rather than "oxidation state" because it is more common in the literature devoted to heterogeous catalysts) has become possible only in the last two decades as a result of the application for this purpose of spectroscopic methods, in the first place the EPR and ultraviolet spectroscopic methods. Fairly reliable methodological procedures have now been developed for the detection of surface CU ions and for the investigation of their electronic and geometrical structures. Many detailed investigations of their properties have been made. This review is devoted to a systematic account and a survey of studies on these lines.

The first investigations of heterogeneous catalysts containing transition metal ions by the EPR and optical spectroscopic methods date back to 1950's. The application of these methods showed that, with their aid, it is possible to obtain sufficiently reliable information about the coordination, valence, and phase states of the transition metal ions in the bulk of the catalysts. On the other hand, the study of surface ions has encountered appreciable difficulties due mainly to the following two factors. Firstly, the number of surface ions is frequently much smaller than the total number of ions in the catalyst. It is therefore almost impossible to study them by the above spectroscopic methods owing to the background of the ions in the bulk of the catalysts. Secondly, since the coordination sphere of the surface CU ions is greatly distorted as a result of the removal of one or several ligands, the spectra are more difficult to interpret than those of ions in a more symmetrical environment. Even when a distinct spectrum is obtained the question whether a surface or a bulk phase ion is responsible for its appearance is likewise not always trivial. The simplest and most reliable experimental criterion for the assignment of ions to surface CU ions is their accessibility at low

temperatures to adsorbable molecules which behave as typical ligands, for example water, carbon monoxide, ammonia, etc. When these molecules are adsorbed, they enter the first coordination sphere of the CU ions, altering their coordination environment, which is reflected by a change in the parameters of the optical and EPR spectra. However, in this case the assignment of an ion to surface ions is not always evident, because such changes may be induced by other processes, for example, by the hydrolysis of the layer of catalyst near the surface, or by a change in the oxidation state of the ion due to the outer-sphere electron transfer to a molecule adsorbed at a fairly long distance from the given ion. As a rule, only a combined study of the properties of the catalyst surface therefore makes it possible to solve the problem of the assignment of a particular spectrum to surface CU ions.

The interaction of adsorbed molecules on CU ions with formation of surface complexes can proceed without change in the valence state of the CU ions and also with a change in this state. Complexes of the first type are formed as a rule when molecules which are typical ligands in homogeneous complexes and have no oxidation-reduction properties under the adsorption conditions are adsorbed. The complexes of the second type, involving a change in the oxidation state of the CU ions, are particularly characteristic of oxidant molecules ($O_2$, $N_2O$, $SO_2$, etc.). Electron transfer from the ion to the adsorbed molecule with formation of radical-anions, stabilised in the coordination sphere of the CU ions, takes place fairly frequently in this case. The structure and properties of such radical species have been studied vigorously by EPR,[5–9] because they play a significant role in many catalytic processes. Examination of studies of the radical-anions requires a special review and here we shall therefore consider them only to demonstrate the ability of the CU ions to form such charge-transfer complexes and attention will be concentrated on complexes of CU ions of the first type.

Deposited catalysts, i.e. catalysts prepared by depositing in one way or another transition metal compounds onto a support, in which the concentration of the CU ions is relatively high, are most convenient for investigation. However, in this case too the deposited ions can form either a solid solution in the carrier lattice or they can give rise to microcrystals of the deposited substance, i.e. they may exist in the bulk of the solid and not on the surface. During the last decade, zeolite catalysts into which transition metal ions have been introduced by ion exchange have come to be widely used. The study of such catalytic systems, as well as deposited catalysts, can yield rich information about the properties of the CU ions. The EPR and ultraviolet spectroscopic studies of CU ions in zeolites have been reviewed.[10,11]

## II. METHODOLOGICAL CHARACTERISTICS OF THE APPLICATION OF THE EPR AND ULTRAVIOLET SPECTROSCOPIC METHODS FOR THE STUDY OF HETEROGENEOUS CATALYSTS

The application of the ultraviolet spectroscopic method to the investigation of solid catalysts has a number of characteristic features which distinguish it from its application to liquids. This is due to the fact that, for catalysts which are usually finely dispersed systems, light is appreciably scattered and reflected which hinders and in many cases virtually precludes the observation of their transmission spectra. In order to diminish light scattering, one can place the disperse solid in a medium, for example, liquid paraffin, with the same refractive index, and then measure the absorption spectra. However, it is much more convenient to deduce the absorption spectrum from the information carried by the light scattered by the specimen. For this purpose, it is necessary to measure the diffuse reflectance spectra. The method of measurement of such spectra is relatively simple and has therefore come to be widely used nowadays.[12–17]

The reflectance spectrum of the specimen is usually obtained from measurements of the relative diffuse reflectance coefficient $R_{diff}$ as a function of the wavelength. The quantity $R_{diff}$ is defined as the ratio of the intensities of the light subjected to diffuse reflectance by the specimen and a standard. Strongly reflecting white powders, for example MgO, $SiO_2$, $MgSO_4$, $Al_2O_3$, and NaCl are used as standards. Kubelka and Munk and, independently of them, Gurevich, Girin, and Stepanov proposed an equation for the dependence of $R_{diff}$ on the concentration of the absorbing centres in the specimen $c$ and on their extinction coefficient $\varepsilon$:

$$(1-R_{diff})^2/2R_{diff} = S\varepsilon c,$$

where $S$ characterises the properties of the medium and is independent of the light wavelength.[12–15] Since the quantity $S$ is usually unknown, it is impossible to determine $\varepsilon c$ exactly. However, the position of the absorption maximum (the maximum value of $\varepsilon$) can be determined from measurements of $R_{diff}$, i.e. it is possible to obtain the same information about the energy of the optical transitions as in the measurements of absorption spectra.

The application of the EPR method to the study of catalysts does not entail any special methodological difficulties, because it is suitable for the study of substances in any state of aggregation. The spectra are usually measured in quartz bulbs, which makes it possible to subject the specimen to different types of treatment, including a high-temperature treatment, and to carry out adsorption and other operations in the absence of air or in a controlled atmosphere. The interpretation of the EPR spectra is sometimes difficult because polycrystalline or amorphous specimens have more complex spectra than single crystals and their elucidation requires special procedures.[18–20] The theoretical principles of the EPR method have been sufficiently fully described in various monographs, for example Refs.19–22.

## III. IONS OF METALS IN THE FIRST TRANSITION SERIES

We shall describe the available data in order of increasing atomic number of the transition element forming part of the catalyst. This method of exposition constitutes in our view the most rational way of giving a systematic account of the literature data.

### 1. Titanium Ions

The EPR and optical spectroscopic studies on surface titanium CU ions published hitherto refer mainly to $Ti^{3+}$ with the electronic configuration $(A)\ (3d)^1$, where $(A)$ is a completed electron shell. Titanium dioxide in two modifications (anatase and rutile) and deposited catalysts have been studied.

At the beginning of the 1960's it was shown that the adsorption of oxygen at room temperature on partly reduced anatase specimens leads to the appearance of a signal due to adsorbed oxygen radical-anions in the EPR spectrum.[23,24] The observation of this phenomenon led to a whole series of studies by different investigators[25–30] of the coordination

and valence states of the titanium ions on the surface of partly reduced $TiO_2$ and of their role in the formation of radical-anions. In a detailed investigation of specimens of partly reduced anatase, Kazanskii and co-workers observed in the EPR spectra, measured at the temperature of liquid nitrogen, a broad absorption line, whose form depended on the degree of reduction of the specimens.[25] In the spectra of specimens subjected to a vacuum heat treatment in the range 300–500 °C, the form of this line is determined by the anisotropy of the $g$-factor ($g_\perp = 1.97$ and $g_\parallel = 1.90$). On the basis of the values of the $g$-factors for the line and its disappearance when oxygen is adsorbed, the authors concluded that the line is due to surface tetrahedrally coordinated $Ti^{3+}$ ions.

A broad line has been frequently observed in the EPR spectra of partly reduced anatase at the temperature of liquid nitrogen also in other investigations.[26–28] The authors likewise attributed this to surface $Ti^{3+}$ ions. However, some workers[26,27] believe that the $Ti^{3+}$ ions responsible for its appearance exist in a tetragonal ligand field, i.e. are surrounded by five or four lattice oxygen ions forming a square pyramid or a square respectively. These coordinations arise from the initial octahedral environment of titanium ions when one or two lattice oxygen ions are removed in the reduction process. A specific type of coordination of the surface $Ti^{3+}$ ions of anatase was not discussed by Cornaz et al.,[28] but they noted that there are three sites in the coordination sphere of titanium ions.

Partly reduced specimens of another modification of $TiO_2$ (rutile) have also been investigated by EPR.[29,30]. A signal with $g_\perp = 1.959$ and $g_\parallel = 1.946$ appeared in the spectra of specimens subjected to a vacuum heat treatment at 500 °C (measurements at 77, 4.2, and 1.6 K). Analysis of the $g$-factors and spin–lattice relaxation times at the temperature of liquid helium and also the disappearance of the signal following the adsorption of oxygen showed that the signal is due to surface CU $Ti^{3+}$ ions tetragonally coordinated. Such coordination arises as a result of the abstraction of one or two oxygen ions located at a distance of 1.988 Å from the titanium ion (the remaining four oxygen ions are at a distance of 1.944 Å). The authors suggest that the width of the signal at 4.2 K is determined by the spin–lattice relaxation time and not by the dipole–dipole interaction and on this basis they concluded that the distance between the $Ti^{3+}$ ions should be not less than 6 Å.

In later studies[31–33] it was concluded from the analysis of the EPR signal parameters that the CU $Ti^{3+}$ ions on the rutile surface are most probably formed when one oxygen ion is removed from the first coordination sphere of the initially octahedrally coordinated titanium ions. Fluorinated rutile specimens have also been studied[31–33] and it has been shown that CU $Ti^{3+}$ ions involved in a square-pyramidal coordination, in the coordination spheres of which the oxygen ions have been partly replaced by fluoride ions, are present on the surface of such specimens. In these studies the EPR signal was assigned to surface CU ions not only from the analysis of the magnetic resonance parameters but also on the basis of the study of the formation of complexes by the CU ions with water and ammonia molecules. When the molecules of these substances were adsorbed at room temperature, they entered the first coordination sphere of the CU $Ti^{3+}$ ions, altering their coordination to octahedral, which changed the corresponding EPR parameters. After the vacuum heat treatment at 400 °C of specimens with adsorbed water molecules, the initial form of the spectrum due to the $Ti^{3+}$ ions and its intensity were restored, and the changes in the signal in repeated adsorption–desorption cycles were found to be fully reversible.

The conditions in the formation of the CU $Ti^{3+}$ ions on the surface of deposited titanium silicate catalysts and their properties were investigated for the first time by Shvets and Kazanskii,[34] who showed that the reduction and subsequent vacuum heat treatment at 500 °C lead to the formation of CU $Ti^{3+}$ ions. In the presence of a high titanium content in the specimens (≥2 wt.%) the ions exist mainly in square-pyramidal coordination, while in the presence of low titanium content (~0.2 wt.%) they exist in tetrahedral coordination. Both these and other ions serve as centres for the adsorption of the molecules of typical ligands, for example, water.

The surface $Ti^{3+}$ ions of silica gel have been obtained[35] by the reaction of $Ti(CH_2C_6H_5)_4$ with hydroxy-groups. It has been shown by EPR that this involves the formation of $(-O-)_2TiR$ and $(-O-)TiR_2$ complexes, in which titanium ions can apparently be regarded as coordination unsaturated. The adsorption of $H_2$ and $C_2H_4$ entails the formation of complexes with a Ti–H bond.

The method of optical spectroscopy in diffusely scattered light has been used[36] to study the coordination state of surface quadrivalent titanium ions deposited on the surface of silica gel by the reaction of $TiCl_4$ with OH groups. Analysis of the position of the absorption band enabled the author to attribute it to octahedrally coordinated $Ti^{4+}$ ions formed as a result of the interaction of the initial CU tetrahedrally coordinated $Ti^{4+}$ ions with water molecules.

### 2. Vanadium Ions

Hitherto the most detailed studies have been made of the Cu $V^{4+}$ ions [electronic configuration $(A)\ (3d)^1$]. $V_2O_5$ has been studied widely by EPR. However, it was not possible to observe effects associated with the formation of surface CU ions. Only recently it has been shown[37] that tetrahedrally coordinated $V^{4+}$ ions, whose EPR spectrum is not observed at room temperature, are formed on the surface of $V_2O_5$ subjected to a vacuum heat treatment at temperatures up to 200 °C. At the same time $V_2O_5$ contains also $V^{4+}$ ions in square-pyramidal coordination, although it is not clear whether they are present in the bulk phase or on the surface of the catalyst. It has been concluded that the tetrahedrally coordinated ions serve as centres for the adsorption of formic acid molecules. Following adsorption, the tetrahedral coordination of the $V^{4+}$ ions changes to square-pyramidal and their spectrum is observed at room temperature.

The CU ions on the surface of different deposited catalysts have been studied in greater detail. It has been shown[38] that the surface of vanadium silicate catalysts reduced *in vacuo* at 500 °C contains tetrahedrally coordinated $V^{4+}$ ions. The authors arrived at this conclusion by comparing the EPR spectra of the reduced catalysts measured at 20 K and of $VCl_4$ in which the $V^{4+}$ ion is tetrahedrally coordinated to chloride ions. The EPR spectrum of the tetrahedrally coordinated $V^{4+}$ ions, measured at room temperature, is greatly broadened and can hardly be observed. It has been shown[38] from the change in the spectrum after the adsorption of water at room temperature that these ions serve as centres for the adsorption of water molecules. After adsorption, the EPR spectrum of the tetrahedrally coordinated $V^{4+}$ ions disappears and is replaced by the vanadyl ion spectrum. This spectrum can be observed both at low and room temperatures. After the adsorption of water molecules, the $V^{4+}$ ions are in square-pyramidal or distorted octahedral coordination where one

of the bonds is shortened, which in fact results in the formation of the vanadyl bond.

Detailed EPR studies[39–42] of the properties of tetrahedrally coordinated CU $V^{4+}$ ions on the surface of $V/SiO_2$ catalysts showed that they adsorb not only $H_2O$ but also $NH_3$, $CH_3OH$, $C_2H_5OH$, $SO_2$, $N_2O$, and CO. Even complexes with the molecules of $N_2$,[39] olefins (for example, propene[43]), and aromatic compounds (for example o-xylene, toluene, and benzene[44,45]) have been observed. The parameters of the EPR spectra of the complexes with hydrocarbons are close to those of the vanadyl complexes.

It has been shown[9,46,47] that the adsorption of $O_2$ on the reduced $V/SiO_2$ catalysts in the temperature range 77–300 K leads to the appearance of two new EPR signals with $g_1 = g_1 = 2.023$, $g_2 = 2.011$, $g_3 = 2.004$, and $g_\perp = 2.026$ ($g_\parallel < g_\perp$), which are due to the adsorbed $O_2^-$ and $O^-$ radical-anions. The $O_2^-$ radical-anions are formed as a result of electron transfer from the CU $V^{4+}$ ions to adsorbed water molecules. The $O^-$ radical-anions are formed on dissociation of $O_2^-$. A hyperfine structure due to one vanadium nucleus is observed in the EPR spectra, which indicates the stabilisation of the radical-anions in the first coordination sphere of the CU vanadium ions. A calculation has been carried out[48] for a model of the adsorption complex formed under these conditions, while in other investigations the reactivity of complexes with charge transfer from the CU ion to oxygen was studied in detail by EPR.[49–52]

Tetrahedrally coordinated $V^{4+}$ ions are formed on the surface of $V/SiO_2$ catalysts not only on thermal reduction but also on photoreduction at 77 K in an atmosphere of $H_2$.[53,54] Two absorption bands, at 13 100 and 19 500 $cm^{-1}$, correspond to these ions in the diffuse electronic spectra, which indicates an appreciable distortion of their tetrahedral coordination. It is of interest that the photoreduction in an atmosphere of CO leads to the formation of CU $V^{3+}$ and not $V^{4+}$ ions. These ions cannot be detected by EPR at 77 K and above, but they have been reliably identified from the optical spectra (absorption bands at 11 800, 17 000, and 23 000 $cm^{-1}$). The $H_2O$, $NH_3$, CO, and $C_2H_4$ molecules can enter the first coordination sphere of the $V^{3+}$ ions with formation of surface complexes.

The coordination states of the ions in the $V/Al_2O_3$ and $V/SiO_2$ catalysts are different. The characteristic vanadyl ion signal has been observed in the EPR spectra of alumino-vanadium specimens.[38] The adsorption of water molecules does not alter its form. It was concluded that the ions are present in a layer of $\gamma$-$Al_2O_3$ near the surface and have square pyramidal coordination. Other workers[39,55,57] arrived at an analogous conclusion. However, one should note that, since the EPR parameters of the $V^{4+}$ ions in "vanadyl" coordination are determined mainly by the presence of a shortened metal–oxygen bond, it is difficult to reach a conclusion from the data obtained whether such square pyramidal ions, even if they are located on the surface, can serve as centres for the adsorption of polar molecules. Some increase in the intensity of the signal due to vanadyl ions has been observed after the adsorption of water and certain other substances. This can be explained by the fact that, before adsorption, CU $V^{4+}$ ions were present on the surface in a non-vanadyl type of coordination. The results of a study[57] where bands corresponding to vanadyl ions and tetrahedrally coordinated $V^{4+}$ ions were found in the EPR spectra of deposited aluminovanadium and vanadium–magnesium catalysts are of interest.

The coordination state of quadrivalent vanadium ions deposited on the surfaces of cabosil, $\gamma$-$Al_2O_3$, gibbsite, and boehmite [modifications of $Al_2O_3$] has also been investigated by allowing the surface OH groups to react with $VCl_4$.[58] When it is adsorbed on cabosil heated to 700 °C, $VCl_4$ reacts with only one OH group, forming tetrahedrally coordinated $V^{4+}$ ions. $V^{4+}$ ions which are both tetrahedrally coordinated and having the vanadyl coordination are formed on rehydrated cabosil. The ions on the $\gamma$-$Al_2O_3$ surface always have the vanadyl coordination, while on boehmite the authors observed a complex spectrum with three $g$-factors, apparently indicating the formation of ions involved in a strongly distorted octahedral coordination.

CU $V^{4+}$ ions have been observed and investigated on the surface of vanadium–zirconium catalysts.[59] A distinctive feature of these systems is that both CU ions and surface complexes with adsorbed water, methanol, and ammonium molecules have EPR spectra characteristic of the vanadyl coordination. The formation of complexes is manifested by a change in the magnetic resonance parameters, in the first place in $A_\perp$. Thus the CU $V^{4+}$ ions of the vanadium–zirconium catalysts are apparently involved in a square-pyramidal coordination.

Data concerning the existence of surface CU $V^{3+}$ ions on vanadium–phosphorus catalysts deposited on silica gel have been published.[60] These ions form surface complexes with water molecules. The subsequent adsorption of oxygen at room temperature leads to their oxidation to $V^{4+}$, which is manifested by a sharp increase of the EPR signal intensity.

The $V^{5+}$ ions, having the electronic configuration $(A)(3d)^0$, are non-paramagnetic and cannot be detected by EPR. The optical reflection and luminescence spectroscopic methods have therefore been used to detect the CU ions and to investigate their properties.[61–63] It has been shown that the CU $V^{5+}$ ions on the surfaces of vanadium silicate catalysts have distorted tetrahedral coordination (one of the vanadium–oxygen bonds is appreciably shortened and constitutes the vanadyl bond) and are capable of adsorbing various molecules ($H_2O$, $NH_3$, alcohols, etc.). Tetrahedrally coordinated CU $V^{5+}$ ions have been detected by reflection spectroscopy also on the surfaces of vanadium silicate catalysts prepared by molecular layer-by-layer deposition.[64–66] It has been suggested[67] that the presence of tetrahedrally coordinated CU vanadium ions on the surface of silica gel is responsible for the selectivity of the oxidation of propene to acrolein.

### 3. Chromium Ions

The extensive application of chromium-containing catalysts in various industrial processes (polymerisation of ethylene, dehydrocyclisation, dehydrogenation etc.) led to the publication of a large number of studies on such catalysts by EPR and optical spectroscopic methods. Although the coordination state of the chromium ions on the catalyst surface has been discussed in many communications, much less attention has been devoted to the direct investigation of the formation and properties of CU ions. We shall examine them in order of decreasing oxidation state of the chromium ions.

The $Cr^{6+}$ ions have no unpaired electrons and therefore do not give rise to an EPR signal. However, they have an intense absorption band in the near ultraviolet due to a ligand-to-cation charge-transfer transition. When $Cr^{6+}$ ions are deposited on silica gel and aluminosilicate, dichromate ions are formed,[68] while their deposition on $\gamma$-$Al_2O_3$ leads to chromate ions.[68,69] It has been shown[70–72] that chromate ions are present together with dichromate ions on the surface of silica gel.

When deposited chromium catalysts are heated in air or *in vacuo*, $Cr^{5+}$ ions are formed, which were first observed by EPR.[73–76] The amount of $Cr^{5+}$ ions in catalysts subjected to a high-temperature treatment *in vacuo* or in oxygen is

usually several per cent relative to the total deposited chromium.[73,75–79] The remaining chromium ions exist mainly in the hexavalent state. There is also several per cent of ions in the tervalent state.

The EPR spectrum of the $Cr^{5+}$ ions in aluminochromium catalysts consists of an almost isotropic line with a width of approximately 40–50 G and $g = 1.96$. When the spectrum is measured in the 8 mm range, the line becomes anisotropic.[76] On the basis of the broadening of the line after the adsorption of oxygen, it has been concluded[77] that it is due to surface ions. It has been shown[38] that the $Cr^{5+}$ ions in the aluminochromium catalysts subjected to a vacuum heat treatment at 500 °C are stabilised in the form of chromyl ions $(Cr{=}O)^{3+}$ in truncated square pyramidal coordination.

The reflection spectra of the aluminochromium catalyst activated at 300 °C consist of three bands with absorption maxima at 14 000, 18 200, and 22 700 $cm^{-1}$.[80,81] These spectra are close to those of various complexes containing the chromyl ion $(Cr{=}O)^{3+}$. In view of this finding and also from the comparison of the experimental $g$-factors of the EPR signal ($g_\perp = 1.97$ and $g_\parallel = 1.95$), measured in the 8 mm range, with the values calculated theoretically the authors concluded that the $Cr^{5+}$ ions on the surface of the aluminochromium catalysts are stabilised in square-pyramidal coordination. The optical and EPR spectra of the catalysts activated at 300° and 500 °C are different. It was concluded that the $Cr^{5+}$ ions can exist on the surfaces of the aluminochromium catalyst in two coordinations—tetrahedral and square-pyramidal. The number of centres of each type depends on the temperature of the heat treatment of the specimens.

EPR studies on chromium(V) ions in catalysts on other carriers have shown that the absorption line form for these ions depends on the nature of the carrier, indicating different types of coordination of the $Cr^{5+}$ ions on the surfaces of different carriers. A theoretical calculation led Aleksandrov et al.[82] to conclude that the ions in a deposited chromium silicate catalyst are stabilised on the surface of silica gel in oxygen tetrahedra. The tetrahedra are distorted, leading to anisotropy of the $g$-factor of the EPR signal. By measuring the EPR spectra in the range from room temperature to 20 K, it was possible to confirm this conclusion and also to show that only less than 1% of the $Cr^{5+}$ ions have square-pyramidal coordination.[38] Measurements of the integral intensities of the spectra have shown that both at room temperature and at the temperature of liquid nitrogen only a proportion of the ions are manifested. The explanation is that the catalyst surfaces contain tetrahedrally coordinated $Cr^{5+}$ ions distorted in different ways. The distortions of the tetrahedra lead to differences in the spin–lattice relaxation times of the $Cr^{5+}$ ions, which entails in its turn a different dependence of the width of the signals on the temperature of measurement of the EPR spectra. As a result, some of the $Cr^{5+}$ ions give rise to absorption lines in the measurement at room temperature and even at the temperature of liquid nitrogen which are so broad that they cannot be observed by EPR. Thus measurements of the concentration of chromium ions in chromium silicate catalysts from the intensities of the EPR spectra must be carried out at least at the temperature of liquid hydrogen.

Measurements of the optical spectra of deposited chromium silicate catalysts have also confirmed that the $Cr^{5+}$ ions are stabilised on the surface in oxygen tetrahedra. These investigations were first made by Pecherskaya and Kazanskii.[80,81] They observed that the optical spectra of the catalyst and the compound $Sr_5(CrO_4)_3OH$, in which the $Cr^{5+}$ ions are tetrahedrally coordinated, are identical. Later these conclusions were confirmed in other investigations.[71,72]

Studies on chromium oxide catalysts where aluminosilicates are used as carriers have shown that $Cr^{5+}$ ions in both tetrahedral and square-pyramidal coordination are formed on the surface, i.e. ions characteristic of chromium silicate and aluminochromium catalysts.[83,84]

We shall now consider the results of EPR and optical spectroscopic studies of the interaction of adsorbed molecules with surface $Cr^{5+}$ ions. Detailed EPR investigations of the character of the interaction of water and ammonia molecules with tetrahedrally coordinated CU $Cr^{5+}$ ions on the $SiO_2$ surface have been carried out.[38] Analysis of the EPR spectra at 20 K has shown that the adsorption of $H_2O$ and $NH_3$ at room temperature leads to the formation of $Cr^{5+}$ ions in square pyramidal coordination. For specimens activated at 500 °C, the ratio of the $(CrO_4)^{3-}$ (tetrahedron) and $(Cr{=}O)^{3+}$ (square pyramid) signal intensities was 100; after the adsorption of $H_2O$ and $NH_3$ for 1 h at room temperature, the $(CrO_4)^{3-}$ signal intensities were negligibly small, while the $(Cr{=}O)^{3+}$ signal intensities were 4 and 140 respectively. Thus the adsorption of $H_2O$ molecules at room temperature leads to the disappearance of most of the $Cr^{5+}$ ions. The phenomenon is caused by the disproportionation of the $Cr^{5+}$ ions to $Cr^{6+}$ and $Cr^{4+}$ ions when water is adsorbed.

The adsorption of water also leads to a fourfold increase of the concentration (compared with the initial value) of $Cr^{5+}$ ions having square-pyramidal coordination. After $NH_3$ adsorption the concentration of the $Cr^{5+}$ ions exceeds the initial value, which is apparently associated with the partial reduction of the $Cr^{5+}$ [$Cr^{6+}$?] ions by ammonia. Thus the tetrahedrally coordinated $Cr^{5+}$ ions on the $SiO_2$ surface serve as centres for the adsorption of polar molecules, i.e. they are CU ions. The adsorbed molecules enter the first coordination sphere of the CU ions and form surface complexes.

Changes in the coordination state of $Cr^{5+}$ ions on the $\gamma$-$Al_2O_3$ surface, occurring on adsorption of various molecules, are much more difficult to observe. However, in this case too it has been possible to establish[38] that the adsorption of $H_2O$ molecules decreases the anisotropy of the absorption line due to ions with a square-pyramidal coordination. Measurement of the intensities of these spectra in the range from room temperature to 20 K showed that Curie's law holds in both cases. It was therefore concluded that both before and after the adsorption of $H_2O$, the $Cr^{5+}$ ions forms a chromyl bond with one of the oxygen ions in the catalyst lattice.

The formation of complexes by the adsorbed molecules of water, ammonia, alcohols, and aldehydes with the CU $Cr^{5+}$ ions has also been observed in other studies.[85–87] The EPR spectra of the complexes are characteristic of $Cr^{5+}$ ions with a shortened chromyl bond. Thus in all cases the chromium ions in such complexes have a distorted octahedral or square-pyramidal coordination.

The reduction of the deposited chromium oxide catalysts in $H_2$ or CO leads to the disappearance of the absorption lines from the optical spectra and of the EPR signals characteristic of the $Cr^{6+}$ [sic] and $Cr^{5+}$ ions. The EPR spectrum of the reduced deposited aluminochromium catalysts consists of a superposition of a very broad asymmetric line in the range 1500–1800 G ($\delta$-phase) and a symmetrical line with $g \cong 2$ ($\beta$-phase).[76] The $\delta$-phase consists of magnetically isolated $Cr^{3+}$ ions in an axial electric field (apparently in the field of a distorted octahedron). The broad symmetrical line is due to the $Cr^{3+}$ ions forming a magnetically concentrated system. The $Cr^{3+}$ ions of the $\beta$-phase apparently form clusters in which there is a fairly intense exchange and dipole–dipole interaction between the ions. However, the structure of the $\beta$-phase differs from that of $Cr_2O_3$ and is

closer to the chromium oxide gel, which is paramagnetic at room temperature.

When oxygen is admitted at room temperature, the intensity of the EPR line due to the δ-phase diminishes and the EPR signal characteristic of the $Cr^{5+}$ ions appears.[76,88,89] The intensity of the δ-phase signal does not change under these conditions, which shows that some of the $Cr^{3+}$ ions of the β-phase are present on the catalyst surface.

The properties of surface CU ions in reduced aluminochromium catalysts have been studied in greater detail in other investigations.[90–92] It follows from the analysis of the optical spectra of the reduced specimens containing adsorbed water that all the $Cr^{3+}$ ions are involved in octahedral coordination. The desorption of water at 500 °C alters both the optical and EPR spectra. The width of the β-phase line in the EPR spectra increases from 750 to 1070 G. After the adsorption of water at room temperature, the line width diminished and returned to the initial level. The adsorption of methanol at room temperature likewise entails an analogous effect. In contrast to this, the adsorption of ammonia does not induce narrowing of the β-phase absorption line. The broadening of the line on desorption of water was accounted for by the diminution of the indirect exchange interaction via the $O_2$ ions as a consequence of the formation of CU $Cr^{3+}$ ions in a coordination sphere of which one or several oxygen atoms are missing. On adsorption, polar molecules enter the coordination spheres of all the ions and, when the adsorbed molecule contains oxygen atoms, the exchange interaction intensifies and the EPR line becomes narrower.

Measurements of the optical spectra of the aluminochromium catalysts agree well with EPR data.[91,92] After the desorption of water, maxima at 10500, 28800, and 31200 $cm^{-1}$, corresponding to $Cr^{3+}$ ions with square-pyramidal coordination, appear together with the signals of octahedrally coordinated $Cr^{3+}$ ions. The adsorption of ammonia and methanol shifts the absorption maxima of the CU $Cr^{3+}$ ions with square-pyramidal coordination to the short-wavelength region. These effects are caused by the formation of surface complexes with a distorted octahedral coordination. It is of interest to note that the CU $Cr^{3+}$ ions with square-pyramidal coordination form complexes with ethylene and benzene on the surface of aluminochromium catalysts at room temperature.[92]

It has been observed[88] that, after the reduction with hydrogen and subsequent vacuum heat treatment of the deposited aluminochromium catalysts containing 2 wt.% of chromium, the β-phase band virtually disappears from the EPR spectra, reappearing after the adsorption of water at room temperature. The authors assume that the disappearance of the line is associated with the reduction of the $Cr^{3+}$ ions to $Cr^{2+}$ and its appearance after the adsorption of water is due to the oxidation of the $Cr^{2+}$ ions to $Cr^{3+}$. Although there is no doubt about the formation of $Cr^{2+}$ ions in the reduced aluminochromium catalysts,[93–95] nevertheless the increase of the intensity of the EPR band due to the β-phase of the $Cr^{3+}$ ions, observed also in the adsorption of methanol,[90–92] is undoubtedly caused, in our view, by its narrowing and the increase of the amplitude as a consequence of the formation of surface complexes, as stated in the discussion just completed, and not by the oxidation of the $Cr^{2+}$ ions by water molecules, which hardly occurs at room temperature.

The complexes of $Cr^{3+}$ ions, deposited on the carrier surface by different methods, as well as the CU ions formed on their decomposition, have been investigated by EPR and optical spectroscopy in several studies. It was shown that the vacuum heat treatment of the complexes $Cr(NH_3)_6^{3+}$, $Cr(H_2O)_6^{3+}$, and several others at 500 °C leads to the formation of CU $Cr^{3+}$ ions, characterised by a structureless absorption in a broad region of the optical spectrum.[96,97] Such CU ions are centres for the adsorption of polar molecules. In the adsorption of water molecules, their coordination returns to the initial octahedral coordination. The study of the adsorption of ethylene on CU $Cr^{3+}$ ions, stabilised on the silica gel surface, has shown that these ions serve as polymerisation centres.[96,97]

Chromium(III) complexes grafted or deposited on the surface have been investigated by optical spectroscopic and EPR methods.[98–100] The high-temperature dehydration of the specimens caused the same broadening of the EPR line as for the aluminochromium catalyst.[90–92] It is caused by the formation of CU ions.[100]

The reduction of deposited chromium silicate catalysts in an atmosphere of CO or $H_2$ leads to the formation mainly of $Cr^{2+}$ ions, in contrast to the aluminochromium systems.[40,93,95,101] The chromium silicate catalyst reduced in CO at 500 °C assumes a blue colour. Its optical spectrum consists of one band with an absorption maximum at 13000 $cm^{-1}$. Absorption bands have not been observed in the EPR spectrum of such a specimen either at room temperature or at the temperature of liquid nitrogen. The adsorption of polar molecules (water or ammonia) at room temperature does not entail the appearance of absorption lines in the EPR spectra, but it does induce a change in the optical spectrum: after the adsorption of water, the absorption maximum undergoes a hypsochromic shift and is observed as 15500 $cm^{-1}$, while after the adsorption of ammonia it occurs at 16400 $cm^{-1}$. The presence of a single absorption maximum in the optical spectra of reduced chromium silicate specimens both before and after the adsorption of polar molecules and the hypsochromic shift of this maximum after adsorption indicate the tetrahedral coordination of the $Cr^{2+}$ ions in the reduced chromium silicate specimen.[40,95] After adsorption at room temperature, the water and ammonia molecules enter the first coordination sphere of the tetrahedrally coordinated CU $Cr^{2+}$ ions without altering their oxidation state and their coordination is built up to the octahedral coordination. It has also been shown that the concentration of $Cr^{2+}$ ions depends on the nature of the reductant and the amount of deposited $Cr^{6+}$ ions.

The CU $Cr^{2+}$ ions on the $SiO_2$ surface are also capable of forming complexes with CO molecules without change in the oxidational state.[101–103] Depending on the pressure and temperature, the adsorption of CO can lead to complexes containing both two molecules and one molecule. The interaction of CU ions with oxygen induces their rapid oxidation, which makes it possible to employ reduced chromium silicate systems for the elimination of traces of oxygen from various gases.[93] Chromium silicate catalysts for the polymerisation of ethylene also contain CU $Cr^{2+}$ ions, which are believed to be the active centres for this reaction.[93,101,104] However, doubts have been cast on this conclusion[96,97] and it has been shown that the active catalyst contains CU $Cr^{3+}$ ions. It has been recently established that both these valence states of chromium ions are active in the polymerisation of ethylene.[105]

CU $Cr^{2+}$ ions on the $SiO_2$ surface can be obtained not only by thermal reduction at high temperatures but also by photochemical reduction in CO at 20 °C.[106] These ions have a tetrahedral coordination and are characterised by the absorption band at 11800 $cm^{-1}$. Photochemical reduction leads to the formation of CU ions which are more uniform as regards coordination than those obtained by thermal reduction. A very interesting property of CU $Cr^{2+}$ ions obtained by photochemical reduction has been noted, namely their ability to undergo a rearrangement of their coordination environment at temperatures above 150 °C, which alters

their optical spectrum and properties. The reduction of the $Cr/SiO_2$ catalyst in CO at the temperature of liquid nitrogen leads to the formation of CU $Cr^{4+}$ ions and not $Cr^{2+}$ ions. Absorption bands due to the *d–d* transitions at 9400 and 17 000 $cm^{-1}$ correspond to these ions. Apparently the existence of $Cr^{4+}$ ions on the catalyst surfaces was demonstrated fairly reliably for the first time by Pershin et al.[106] It has also been shown that the CU $Cr^{4+}$ ions form the complexes $Cr^{6+}.NO^{2-}$ with NO molecules, transferring two electrons to the adsorbed molecule, which leads to the appearance of an EPR signal with $g_{\parallel} = 2.046$, $g_{\perp} = 1.99$, $A_{\parallel}^{N} = 0$ G, and $A_{\perp}^{N} = 10$ G.

The formation of CU $Cr^{2+}$ ions on the surfaces of reduced aluminochromium catalysts has been observed by EPR from the interaction with the adsorbed NO molecules.[107] The adsorption of NO at room temperature led to the formation of the surface complexes $Cr^{+}.NO^{+}$ in a low-spin state as a result of electron transfer from the adsorbed molecules to the CU $Cr^{2+}$ ions.

The formation of CU ions in the vacuum heat treatment of mononuclear and dinuclear complexes of $Cr^{2+}$ ions deposited by ion exchange or grafted on to $SiO_2$, $\gamma$-$Al_2O_3$, and MgO has been investigated.[96,108] The vacuum heat treatment of such complexes on $SiO_2$ leads to the formation of tetrahedrally coordinated $Cr^{2+}$ ions, while on MgO and $\gamma$-$Al_2O_3$ a considerable proportion of the ions are oxidised to $Cr^{3+}$.

In conclusion of this Section, one should note that, in connection with the extensive application of chromium-containing systems as catalysts, the formation and properties of the CU chromium ions in a wide variety of oxidation states has been studied in greatest detail compared with other transition metal ions.

### 4. Manganese Ions

In the EPR study of manganese oxides, both pure and deposited on MgO,[109–112] it was not possible to separate the spectra of the bulk-phase and surface ions, although an increase of the width of the lines due to the $Mn^{2+}$ ions with increase of the specific surface of MgO, caused by the formation of surface ions, has been noted, for example, by Cordishchi et al.[110] Yamamura et al.[111] assumed that they were able to observe surface octahedrally coordinated $Mn^{2+}$ ions in MgO, but later[112] this conclusion was subjected to a fairly convincing criticism.

The $Mn^{2+}$ ions deposited on silica gel surface have been investigated[113,114] by EPR. At a manganese concentration up to several per cent, a broad line due to a magnetically concentrated phase or clusters of $Mn^{2+}$ ions was observed. At low concentrations it was possible to observe a spectrum which was attributed to individual $Mn^{2+}$ ions. The change of their symmetry and coordination compared with a solution has been noted,[114] but in the above studies the formation of CU manganese ions was not investigated under conditions of high-temperature hydration, although their existence on the $SiO_2$ surface can be demonstrated with the aid of the interaction of manganese silicate specimens with oxygen: the presence of such ions permits the use of these systems as sorbents for trace amounts of oxygen in olefins.[115] Yamamura et al.[111] showed only that, in the high-temperature dehydration of octahedral complexes of $Mn^{2+}$ ions deposited on silica gel, their EPR signal disappears, apparently owing to the great band width for the highly distorted surface complexes.

### 5. Iron Ions

The conditions in the formation and properties of CU $Fe^{2+}$ ions on $SiO_2$ have been investigated[116] by diffuse reflectance optical spectroscopy. The formation of CU ions of two types was established: tetracoordinated at activation temperatures *in vacuo* up to 700 °C and bicoordinated at 1000 °C. The former adsorb $H_2O$, NO, and $O_2$ at room temperature, while the latter also adsorb CO, $C_2H_4$, and $N_2$ molecules. It has been noted that the complexes with CO, $O_2$, and $N_2$ are unstable and are readily decomposed after the adsorption of water. The catalytic reactivity of such CU $Fe^{2+}$ ions on $SiO_2$ in the reactions involving the decomposition of NO and its reduction by CO has been studied.[117]

The formation of surface compounds of $Fe^{3+}$ ions in the $Fe_2O_3$–$SiO_2$ and $Fe_2O_3$–$SiO_2$–$Al_2O_3$ catalysts in the high-temperature heat treatment in air have been investigated by EPR and diffuse reflection spectroscopy.[118] It has been observed that water molecules and hydroxy-groups enter the coordination sphere of the surface $Fe^{3+}$ ions.

### 6. Cobalt Ions

The study of deposited cobalt silicate catalysts by the joint application of the EPR and optical spectroscopic methods has shown that the vacuum heat treatment at 700 °C leads to the formation of surface CU $Co^{2+}$ ions in a tetrahedral coordination and that tetrahedra compressed along the trigonal axis are produced.[119] The optical spectra change after the adsorption of $H_2O$ and $NH_3$ molecules at 20 °C, which indicates the formation of complexes with a square-pyramidal or highly distorted octahedral coordination.

The optical spectra of specimens obtained by impregnating silica gel with aqueous $CoCl_2$ and $Co(NO_3)_2$ solutions and by ion exchange have been compared.[99] It was found that the properties of the surface complexes depend both on the methods of their deposition on the surface and on the nature of the cobalt compound. Thus, whereas the octahedral coordination of the $Co^{2+}$ ion on the catalyst surface, obtained by impregnation with a $Co(NO_3)_2$ solution, does not change after drying at room temperature, nevertheless under the same conditions the octahedral coordination of the $Co^{2+}$ ions obtained from $CoCl_2$ changes to the tetrahedral coordination. The introduction of $Co^{2+}$ ions by ion exchange immediately leads to tetrahedrally coordinated ions. After specimens prepared by impregnation had been heat treated in air at 500 °C, cobalt ions with a tetrahedral coordination are also formed.

Much attention has been devoted to the investigation of the state of the cobalt ions deposited on $Al_2O_3$ and MgO.[120–122] Changes have been observed in the optical spectra of tetrahedrally coordinated $Co^{3+}$ ions on the $Al_2O_3$ surface after the adsorption of propene.[120] On the MgO surface, some of the $Co^{2+}$ ions are in square-pyramidal coordination, which changes to distorted octahedral coordination on adsorption of $NH_3$.[122]

The surface CU $Co^{2+}$ ions have been detected by optical spectroscopy also in mixed Co–Mo–$Al_2O_3$ catalysts.[123] The changes in the spectra after the adsorption of CO, $H_2O$, thiophen, and pyridine indicate the localisation of the main bulk of the ions in the oxygen tetrahedra. A small proportion of the $Co^{2+}$ ions are present on the surface in a trigonal coordination. Analysis of the optical spectra showed that the presence of the $MoO_3$ phases is essential for the formation of such CU trigonally coordinated ions.

### 7. Nickel Ions

In one of the first studies of nickel ions in catalysts by optical spectroscopy,[124] it was shown that the spectrum of dispersed NiO, obtained *in vacuo*, resembles the spectrum of the complex $Ni(H_2O)_6^{2+}$. The absorption of $O_2$ leads to the same changes in the spectra of the specimens as the introduction of $Li^+$ ions. On this basis, it has been suggested that the effect of $O_2$ is associated with the conversion of some of the $Ni^{2+}$ ions into $Ni^{3+}$. The adsorption of $H_2$ and CO leads to the partial reduction of the oxide and the formation of $Ni^+$ ions. Klier[124] was unable to establish whether the $Ni^+$ and $Ni^{3+}$ ions formed on adsorption are present on the surface layer of NiO or in its layer next to the surface.

Much attention has been devoted in the literature to nickel silicate catalysts. In one of the first studies of these catalysts it was shown[125] that the initial distorted octahedral coordination of the ions in specimens prepared by impregnation with aqueous $NiCl_2$ solutions persists on heating in air up to 500 °C. It was noted that the adsorption of ammonia influences the optical spectra of such specimens albeit fairly weakly. The coordination of the $Ni^{2+}$ ions remains octahedral after adsorption. Conditions for the formation of CU $Ni^{2+}$ ions on the $SiO_2$ surface were found in subsequent investigations.[126] It was shown that the ions are most likely to have distorted tetrahedral coordination and serve as centres for the adsorption of polar molecules.

Measurements of optical reflectance spectra somewhat later[127] led to the conclusion that the $Ni^{2+}$ ions on the $SiO_2$ surface after evacuation at 1000 °C have a coordination number of two and their coordination sphere can therefore include up to four adsorbed molecules. The formation of surface complexes with CO, $C_2H_4$, NO, and $NO_2$ molecules have been observed. One should note that the possibility of such low coordination of surface ions (with a coordination number of two) requires, in our view, more rigorous evidence, although the existence of CU $Ni^{2+}$ ions and their complexes on the $SiO_2$ surface is not in fact open to doubt.

Using the EPR method, the interaction of surface $Ni^{2+}$ ions with anthracene and diphenylpicrylhydrazine to form charge-transfer complexes has been investigated by EPR.[128–130] It has been suggested that anthracene is adsorbed on $Ni^{2+}$ ions with tetrahedral coordination.

Together with the traditional method for the preparation of deposited catalysts by impregnation with inorganic nickel salts, the catalysts have been prepared by the interaction of bis-π-allylnickel with $SiO_2$.[131] It has been established that, when the specimens are heated in $O_2$ above 300 °C, the organic ligand is fully oxidised and CU $Ni^{2+}$ ions in a state with a low symmetry are formed. The exact coordination state could not be established.

The formation of CU nickel ions on MgO has also been investigated by EPR and optical spectroscopy,[132,133]. It has been observed that the intensity of the EPR signal due to the $Ni^{2+}$ ions involved in an octahedral coordination increases after the adsorption of $H_2O$, $NH_3$, and HBr molecules at 20 °C. This was caused by the presence on the surface of CU $Ni^{2+}$ ions involved in a square-pyramidal or tetrahedral coordination, which were undetectable by the EPR method before the adsorption. Analysis of the optical spectra led the authors to give preference to the square-pyramidal coordination.[133]

On reduction of the $Ni/SiO_2$ catalyst by ultraviolet light in $H_2$ at 77 K, the formation of CU $Ni^+$ ions with distorted tetrahedral coordination, containing an $H_2$ molecule in the coordination sphere, was observed.[134] Their EPR spectrum is characterised by the $g$-factors: $g_1 = 2.015$, $g_2 = 2.30$, and $g_3 = 2.64$. After vacuum heat treatment at 520 K, the coordination environment of these ions changes, as shown by the change in the $g$-factor. The CU $Ni^+$ ions form complexes with the adsorbed $O_2$, $H_2O$, $NH_3$, and CO molecules, complexes with one, two, and three CO molecules being present in the last case. At a low temperature, even $N_2$ molecules can enter the coordination spheres of the CU $Ni^+$ ions.

The nickel ions deposited on the silica gel surface can be reduced to the metallic state. Examination of studies on such catalysts is outside the framework of the present review. Nevertheless we would wish to note an interesting study[135] in which the poisoning of a nickel silicate catalyst in the course of the hydrogenation of butene was investigated by ultraviolet spectroscopy and it was shown that this entails the formation of surface complexes of nickel with hydrogen sulphide and the hydrocarbon. These complexes can be extracted from the catalyst and the spectra of the solution and the surface complex are analogous.

### 8. Copper Ions

The EPR study of $Cu^{2+}$ ions deposited on $SiO_2$ by impregnation with an aqueous $Cu(NO_3)_2$ solution showed that CU $Cu^{2+}$ ions in different coordination environments, particularly in distorted tetrahedral coordination, are formed on vacuum heat treatment at 500 °C.[136] Some of the CU $Cu^{2+}$ ions cannot be detected at all by EPR at 77 K apparently owing to the short spin–spin lattice relaxation time. The $H_2O$, $NH_3$, $C_5H_5N$, $C_2H_5OH$, and $SO_2$ molecules adsorbed at 20 °C enter the coordination spheres of the CU $Cu^{2+}$ ions and form surface complexes having distorted octahedral coordination. Reactions involving substitution in the coordination spheres of the surface complexes of one set of adsorbed molecules by another have been observed.

The adsorption properties of the CU $Cu^{2+}$ ions on the $SiO_2$ surface after the introduction of copper ions by ion exchange in the form of the $Cu(NH_3)_4^{2+}$ and $Cu(H_2O)_6^{2+}$ complexes have been investigated.[137,138] It was shown that the initial copper complexes lose the coordinated ligand molecules on vacuum heat treatment and form CU $Cu^{2+}$ ions. In the case of specimens prepared by exchange with $Cu(NH_3)_4^{2+}$, tetrahedrally coordinated ions are formed, as in the study of Bogdanov et al.[136] The coordination of the ions in catalysts prepared by exchange with $Cu(H_2O)_6^{2+}$ could not be determined owing to the poor resolution of the EPR spectrum. The adsorption of $NH_3$ and $C_5H_5N$ molecules leads to the formation of tetragonally distorted octahedral complexes of the CU ions. In the adsorption of $H_2O$ two different EPR spectra were observed, which indicates the existence of two types of complexes with different coordination sphere symmetries.

The formation of exchange-linked ion pairs, which possess the properties of CU ions, i.e. are able to stabilise the different molecules in their coordination spheres, has been observed[139] for deposited copper silicate specimens heated *in vacuo* at 650–950 °C. After the adsorption of polar and non-polar molecules, the ion pairs decomposed and the signals due to the isolated $Cu^{2+}$ involved in different types of coordination were observed in the EPR spectra. Thus octahedral complexes were formed after the adsorption of $NH_3$ and $H_2O$ and complexes involved in coordination corresponding to a truncated octahedron or a tetrahedron compressed along the threefold axis (the EPR spectra have $g_\perp > g_\parallel$) were noted after the adsorption of $C_2H_4$ and CO. The copper ions forming part of the composition of the ion pairs are also capable of forming covalently bound complexes with $O_2$ molecules.

Much attention has been devoted in the literature to aluminocopper catalysts.[140–143] Although it has now been fairly reliably established that the bulk-phase copper ions

in such catalysts have both octahedral and tetrahedral coordination,[144] the coordination state of the surface $Cu^{2+}$ ions has not been determined quite so reliably. On the basis of the analysis of EPR spectra, it has been suggested[145] that the $Cu^{2+}$ ions on the surfaces of oxidised specimens are involved mainly in square-pyramidal coordination. On reduction, some of the $Cu^{2+}$ ions are converted into $Cu^0$ atoms, which form diamagnetic clusters.

In an EPR study of the state of copper in copper-magnesium oxide catalysts,[146] four types of signals were observed, one of which was due to the $Cu^{2+}$ ions in an axial field ($g_\parallel = 2.34$, $g_\perp = 2.058$, $A \cong 150$ G, $B = 28$ G) and was attributed to surface copper complexes with $CO_2$ molecules. This finding indicates the formation of CU $Cu^{2+}$ ions, but their coordination state could not be determined. The appearance of the characteristic EPR spectra after the adsorption of molecules revealed the presence of CU $Cu^{2+}$ ions also on the CuO surface.[147,148] It has been shown that the adsorption of various amines at room temperature entails the appearance of broad signals ($\Delta H \cong 700$–$900$ G), which has been attributed to surface copper complexes. Following the adsorption of $NH_3$, a fairly narrow signal arose with $g$-factors of 2.211, 2.122, and 2.071. The $Cu^{2+}$–$NH_3$ complexes responsible for this signal are stable up to 130 °C. The coordination state of the $Cu^{2+}$ ions before the adsorption was not investigated.

## IV. THE IONS OF METALS IN THE SECOND AND THIRD TRANSITION PERIODS

### 1. Molybdenum Ions

There have been very many fewer studies by EPR and optical spectroscopy of the CU ions of metals in the second and third transition Periods than for the metal ions of the first transition Period. Only molybdenum ions have been studied in fair detail.

In oxidised molybdenum silicate specimens molybdenum exists in a hexavalent state and forms tetrahedral and octahedral complexes according to reflectance spectroscopic data.[149–153] An analogous conclusion was also reached from measurements of luminescence spectra.[62] The surface acidity of the carrier influences significantly the position of the charge transfer band for the $Mo^{6+}$ ions, which is due to the formation of polymeric species incorporating both tetrahedral and octahedral molybdenum ions.[149] It has been suggested that these species are the anions of molybdosilicic heteropolyacid.[154,155]

The reduction of molybdenum silicate catalysts leads to the appearance of an intense EPR signal due to the $Mo^{5+}$ ions with the $A(4d^1)$ electronic configuration.[154–158] Analysis of the spectrum showed that these ions have molybdenyl coordination ($g_\perp = 1.940$; $g_\parallel = 1.882$; $B = 44$ G, $A = 98$ G).[154, 156,157] Furthermore, a considerable proportion of the CU ions on the surface have apparently distorted tetrahedral coordination.[156] At room temperature these ions were not detected in the EPR spectra and at 77 K their signal was superimposed on that due to the molybdenyl ions. On adsorption of $H_2O$, $NH_3$, CO, and other molecules, surface complexes of the CU ions are produced. The EPR spectra indicate their distorted (compressed) octahedral structure. The EPR spectrum of the CU $Mo^{5+}$ ions involved in a low coordination could be observed in a "pure" form on the $Mo/SiO_2$ surface on reduction of the catalyst by exposure to light in an atmosphere of $H_2$ and not thermally.[159] The EPR parameters are as follows: $g_1 = 1.811$, $g_2 = 1.929$, $g_3 = 1.952$, $A_1 = 82$ G, $A_2 = A_3 = 29$ G. The photochemical reduction of the same catalysts in a CO atmosphere leads to the formation of the CU $Mo^{4+}$ ions.[160,161] After the adsorption of NO at 77 K an EPR signal is generated ($g_\parallel = 2.075$, $g_\perp = 1.996$, and $A_\perp^N = 15$ G); it is due to the $Mo^{6+}.NO^{2-}$ complexes, formed as a result of the transfer of two electrons from the CU $Mo^{4+}$ ion to the orbitals of the NO molecule. The unusually strong reductive properties of the CU $Mo^{4+}$ ions, caused by the anomalous coordination, have been observed. For example, the interaction of $Mo^{4+}$ with $CO_2$ at 100 °C entails their oxidation to $Mo^{6+}$ and the liberation of CO molecules to the gas phase. After the reduction of molybdenum silicate catalysts with trimethylaluminium in suspension in toluene, an EPR signal with $g = 1.989$ and seven hyperfine lines having a splitting of 4.9 G, attributed to a surface complex of $Mo^+$ with two toluene molecules, was observed.[162]

The CU $Mo^{5+}$ ions formed on the $SiO_2$ surface on reduction also serve as centres for the adsorption of $O_2$ and $N_2O$ molecules. The adsorption results in the formation of the $O_2^-$ and $O^-$ radical-anions respectively in the coordination spheres of the CU ions.[9,156,163] The $O_2^-$ and particularly $O^-$ radical-ions are highly reactive and can participate in various reactions.[9,50,52,156] Thus $O_2$ and $N_2O$ molecules are activated in the coordination spheres of the CU $Mo^{5+}$ ions, which makes it possible to regard them as active centres for catalytic oxidation reactions.

Oxidised aluminomolybdenum catalysts contain both $Mo^{6+}$ [164, 165] and $Mo^{5+}$ [166] ions. At low concentrations the $Mo^{6+}$ ions have tetrahedral coordination, but, with increase of the molybdenum content, octahedrally coordinated ions are also formed.[164] The reduction of the aluminomolybdenum catalysts leads to the formation of appreciable amounts of $Mo^{5+}$ ions. According to the majority of investigators,[165,167–170] the EPR spectrum indicates their square-pyramidal or compressed octahedral coordination. Some workers[171,172] assume, however, that the $Mo^{5+}$ ions have a distorted tetrahedral coordination. Nevertheless in the majority of studies it has not been possible to observe clear-cut effects indicating the possibility of the stabilisation of polar molecules in the coordination sphere of the $Mo^{5+}$ ions on the $Al_2O_3$ surface and hence to confirm the formation of CU ions. It is noteworthy that the formation of CU molybdenum ions on the surfaces of aluminomolybdenum catalysts has been demonstrated reliably by EPR on the basis of the stabilisation of the $O_2^-$ radical-anions in their coordination sphere.[6,173]

Surface $Mo^{5+}$ ions have been detected by EPR in molybdenum–magnesium systems[173–175] from the broadening of the lines after the adsorption of molecular oxygen at low temperatures. The question of their coordination state has not been ultimately elucidated. Both distorted octahedral and tetrahedral coordinations have been suggested,[173,174] while other workers[175] believe that the ions exist only in distorted octahedral coordination. It has been observed[175] that the adsorption of CO, $C_3H_6$, $N_2O$, $H_2O$, and $NH_3$ molecules increases the anisotropy of the EPR signals by altering $g_\perp$ ($g_\parallel$ is almost constant), which indicates, according to the investigators, a lengthening of the $Mo^{5+} = O$ bond owing to the interaction of the adsorbed molecules with oxygen.

Surface $Mo^{5+}$ ions with square-pyramidal coordination as well as the bulk-phase ions have also been detected in the EPR study of bismuth–molybdenum and zinc–molybdenum catalysts.[176–178] A decrease of the intensity of their EPR signal following the adsorption of water and its increase after the adsorption of propane have been observed.[177] It has been suggested that these changes are caused by the decrease and increase respectively of the spin–lattice relaxation time of the ions as a consequence of the increased degree of symmetry of their environment in the case of $H_2O$ and its decrease in the case of $C_3H_8$.

CU $Mo^{6+}$ and $Mo^{5+}$ ions formed on the surface of carriers in the decomposition of grafted organic or carbonyl complexes of molybdenum have also been studied by EPR and ultraviolet spectroscopy[179,180] and it has been shown that, on the $SiO_2$ and $Al_2O_3$ surfaces, these ions have distorted tetrahedral coordination and the nature of the active centres in catalysts of this type has been discussed.

### 2. Rhodium Ions

It has been shown by EPR that evaluation in the temperature range 200–500 °C of $Rh/SiO_2$ specimens containing $Rh^{3+}$ ions in the initial state leads to the formation of CU $Rh^{2+}$ ions with the $A(4d)^9$ electronic configuration and distorted tetrahedral coordination ($g_1 = 2.68$, $g_2 = 2.22$, $g_3 = 2.00$) as well as octahedrally coordinated $Rh^{2+}$ ions ($g_\parallel = 2.00$, $g_\perp = 2.43$).[181] The fraction of the CU ions increase with increase of the evacuation temperatures and in the specimens heated at 500 °C there are virtually no octahedrally coordinated $Rh^{2+}$ ions. The adsorption of $H_2O$, $NH_3$, $CH_3OH$, and $C_2H_4$ molecules entails the expansion of the coordination sphere of the CU ions and the formation of octahedral complexes of $Rh^{2+}$ ions ($g_\perp = 2.43$, $g_\parallel = 2.00$).

Tetrahedrally coordinated $Rh^{2+}$ ions, formed as a result of the disproportionation of the $Rh^{3+}$ ions *in vacuo* at 500–700 °C, have been observed on the $\gamma$-$Al_2O_3$ surface.[182] CO and $O_2$ molecules can enter their coordination sphere on adsorption, forming paramagnetic surface complexes. The EPR spectra of $Rh/Al_2O_3$ specimens reduced in $H_2$ also show a signal due to the surface complexes of $O_2$ ($g_\parallel = 2.043$, $g_\perp = 2.004$) and CO ($g_\parallel = 2.038$, $g_\perp = 2.003$) with a CU $Rh^0$ atom.[182]

### 3. Palladium Ions

The application of the EPR method to the study of deposited $Pd/Al_2O_3$ [183] and Pd/MgO [184] catalysts made it possible to detect CU $Pd^+$ and $Pd^{3+}$ ions on the surface with the $A(4d)^9$ and $A(4d)^7$ configurations respectively. The CU $Pd^+$ ions are formed on high-temperature activation (reduction, evacuation, partial oxidation, and re-evacuation) of $Pd/Al_2O_3$. Their concentration is several per cent relative to the total palladium content in the specimen. These ions behave as centres for the adsorption of $H_2O$, $NH_3$, CO, and $O_2$ molecules. The EPR spectra of the complexes with CO molecules labelled with the $^{13}C$ isotope show that the complexes contain different numbers of molecules. The adsorption of $O_2$ leads to the formation of the $O_2^-$ radical-anions stabilised in the coordination spheres of the CU palladium ions. The CU $Pd^{3+}$ ions are formed on the Pd/MgO surface under severe oxidation conditions (800 °C). At room temperature *in vacuo* or in an atmosphere of $O_2$ they disproportionate together with the $Pd^+$ ions, present simultaneously in the catalyst, to form $Pd^{2+}$ ions: the CU $Pd^{3+}$ ions are readily reduced in $H_2$ and CO.

### 4. Tungsten Ions

The reduction of deposited $W/SiO_2$ catalysts does not lead to the appearance of any signals in the EPR spectra measured at 77 and 300 K.[185] However, after the adsorption of CO or $NH_3$ on the reduced specimens, intense EPR signals are generated. Their parameters (CO: $g_\perp = 1.901$ and $g_\parallel = 1.784$, $NH_3$: $g = 1.800$ and $g = 1.674$) indicate the formation of surface distorted octahedral complexes of the $W^{5+}$ ions. Consequently, before adsorption, CU $W^{5+}$ ions, undetectable by EPR at 77–300 K owing to their short spin–lattice relaxation time, are present on the surfaces of these catalysts. The adsorption of $O_2$ stabilises the $O_2^-$ radical-anions in the coordination spheres of the CU ions.[179,185]

### 5. Platinum Ions

The EPR method has been used to identify the paramagnetic centres in deposited $Pl/Al_2O_3$ and $Pt/SiO_2$ catalysts.[186] It has been shown that heat treatment of the $Pt/Al_2O_3$ specimens in $O_2$ at 623 K induces the appearance of an intense EPR signal with $g_\perp = 2.222$ and $g_\parallel = 2.046$, which has been attributed to the $Pt^{3+}$ ions with the electronic configuration $A(5d)^7$. The adsorption of $O_2$ entails a decrease of the intensity of this signal and the appearance of signals due to oxygen radicals. It has been concluded that the $Pt^{3+}$ ions are present on the catalyst surface, but their coordination state has not been established. In contrast to $Pt/Al_2O_3$, the formation of paramagnetic platinum ions could not be observed on the $Pt/SiO_2$ catalyst. When $Pt/Al_2O_3$ and $Pt–Ir/Al_2O_3$ catalysts containing chlorine were heated, the formation of paramagnetic CU $Pt^+$ ions, stabilised in the form of the surface $[PtCl_2]^-$ complex, was observed.[187] It has been suggested that the $Pt^+$ ion in this complex is an active centre for the dehydrocyclisation of paraffinic hydrocarbons.

## V. CONCLUSION

The data presented show that electron paramagnetic resonance and optical spectroscopy of diffusely scattered light permit a reliable identification of the formation of CU transition metal ions on the surfaces of catalysts and an investigation of their properties.

It is possible to demonstrate, fairly reliably, tetrahedral coordination of the CU transition metal ions, distorted in different ways, on the silica gel surface. When alumina was used as the carrier, the formation of CU ions in square-pyramidal and tetrahedral coordinations was observed. Thus the coordination state is determined to a large extent by the nature of the carrier. The methods of deposition of the transition elements, their concentration, and the conditions in their activation also play an important role.[60,65,66,127,136,139,153,188,189] The literature data show that the coordination state of the surface ions influences significantly the selectivity and rate of catalytic reactions.[153,158,188–190] The stabilisation of transition metal ions on the catalyst surfaces in an oxidation state atypical for the bulk phase ($Cr^{5+}$, $Cr^{2+}$, $Mo^{5+}$, $Rh^{2+}$, $W^{5+}$, etc.) is also associated with their unusual coordination.

The CU transition metal ions are able to interact with various adsorbed molecules to form surface complexes, which in the case of molecules behaving as typical ligands in solutions, have as a rule a distorted octahedral coordination. There is a possibility of the formation of complexes having a more involved structure, for example, those with olefinic hydrocarbons, $SO_2$, $O_2$, and $N_2O$. It is noteworthy that the stabilisation of polar molecules in the coordination spheres of CU ions in many cases does not apparently reduce solely to the filling of the vacant sites by adsorbed molecules. The coordination environment of the ions also undergoes a rearrangement under these conditions.

The formation of complexes between the adsorbed molecule and the CU ions can lead to an increase of its reactivity. Thus the adsorption of $O_2$ molecules entails in many cases the formation of $O_2^-$ radical-anions stabilised in the coordination sphere of the CU ion. Their reactivity is much higher than that of $O_2$ molecules. On raising the temperature, the

molecules adsorbed in the coordination spheres of the surface CU ions can be both desorbed and can undergo chemical changes as a result of their interaction with the CU ions, as has been demonstrated, for example, in the case of $H_2O$ molecules in the coordination spheres of the $Cr^{3+}$ ions[95] or $N_2O$ molecules in the coordination sphere of the $V^{4+}$ ions.[39,46] There is also a possibility of the substitution of one set of molecules adsorbed in the coordination sphere by another, for example, in the case of the surface copper complexes on $SiO_2$ when ammonia and methanol are adsorbed.[136]

The adsorption of carbon monoxide molecules frequently leads to the formation of surface paramagnetic complexes of the carbonyl type. A weak bond between the CO molecule and the ion, which is ruptured even on evacuation at room temperature, is characteristic of these complexes. On the other hand, the changes in the optical and EPR spectra occurring in such complex formation indicate that, although this type of weak adsorption of CO corresponds to physical adsorption as regards bonding energy, it nevertheless entails significant changes in the electronic state of the adsorption centre—the CU transition metal ion. Consequently it occurs with participation of the electrons of the adsorption centre and constitutes chemical adsorption.

The anomalous, compared with the bulk phase, coordination of the surface CU transition metal ions also leads to a difference in the oxidation-reduction properties [compared with the bulk-phase]. Thus the interaction of the CU $Cr^{2+}$ ions in tetrahedral coordination on the $SiO_2$ surface with oxygen leads to their oxidation to the quinquevalent and hexavalent states even at room temperature, whereas the octahedrally coordinated $Cr^{2+}$ ions are oxidised under these conditions to the tervalent state.[95]

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# Reactions on Catalyst Surfaces under Programmed-heating Conditions

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The temperature-programmed reaction method and the principles of the calculation of the kinetic parameters of the surface stages of a catalytic process have been described. The influence of surface non-uniformity and the limiting stage on the parameters obtained has been examined. The possibility of detecting intermediate products of surface reactions has been analysed.
The bibliography contains 37 references.

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## I. INTRODUCTION

The large number of studies of catalytic processes, including the stages of adsorption, the surface reaction, and desorption, indicate the complexity of the reactions of gases with solid surfaces. Even when catalysts with well characterised surfaces, for example metal single crystals, are used, the interpretation of the data obtained under stationary reaction conditions is extremely difficult. It is therefore natural to study the kinetics and mechanism of these processes by non-stationary methods, in particular the familiar thermal desorption (TD) method, which has been widely used to study the energy parameters of the reaction of simple gases with pure metal surfaces.[1,2] One of the first studies of the use of this method in catalysis was carried out in the 1960's,[3] and since then the number of studies carried out by the TD method has increased continuously.[4-6] The present review examined chiefly work carried out in the 1970's and 1980's, and deals with the problems of the reactions of gases with surfaces of interest for catalysis.

## II. PRINCIPLES OF THE METHOD AND THE CALCULATIONS

### 1. The Temperature-programmed Reaction Method

The temperature-programmed reaction (TPR) or temperature-programmed surface reaction (TPSR) method involves the adsorption of the substance being studied on a catalyst surface under given conditions, the removal of molecules of the original substance from the gas phase, and subsequent heating of the catalyst (usually at a constant rate) with simultaneous analysis of the products liberated at definite time intervals or at different catalyst temperatures. TPSR differs from thermal desorption in that in the first case the adsorbed substances undergo various transformations on the catalyst, that is a surface reaction takes place and the products of the transformation are liberated into the gas phase, whereas in the second case the adsorbed and desorbed species have the same composition. The main experimental approaches can be divided into two groups, depending on the methods used to remove and analyse the products from the gas phase: the chromatographic version,[3] in which the removal of the reaction products and the chromatographic analysis are carried out using an inert carrier gas, and the vacuum version, which originates from the first studies of the thermal desorption of simple gases from metal surfaces,[1,2] and which involves the vacuum treatment of the specimen after adsorption and mass-spectrometric analysis of the desorbed products. In the last case, the experiments can be carried out in closed systems or in flow systems.

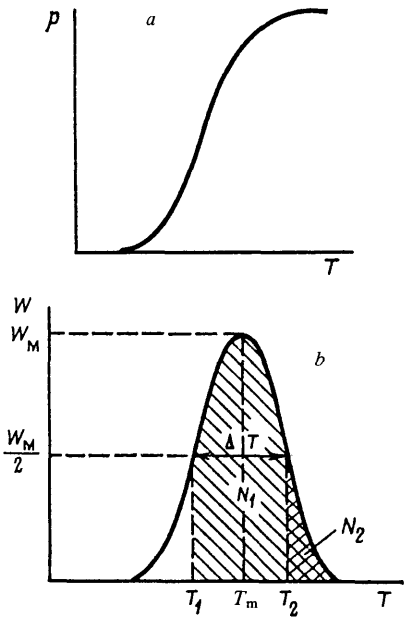



Figure 1. Schematic representation of the desorption curves in closed (*a*) and flow (*b*) systems. The hatched areas correspond to the concentrations of the molecules on the surface at temperatures $T_1$ and $T_2$; $T_m$ is the temperature of the peak maximum.

Fig. 1*a* gives a schematic representation of the temperature dependence of the pressure of the desorbed substances ($p$) in a closed system. Differentiation of the curve in Fig. 1*a* makes it possible to find the dependence of the rate of liberation of the product into the gas phase on time (that is the catalyst temperature). The same dependence (of $W$ on $T$)

can be obtained by carrying out TD and TPSR in a flow system (Fig. 1*b*) at sufficiently high rates of evacuation. Although carrying out the experiments in a flow system lowers the sensitivity of the method, it makes it possible to avoid graphical differentiation, that is to increase the accuracy of the determination of the kinetic parameters; moreover, as a consequence of the decrease in the pressure in the system, it is possible to neglect the re-adsorption of the desorbed gases. For a flow system, the equation for the material balance of the product liberated in the gas phase can be written as follows:

$$V\frac{dp}{dt} = W - ps \qquad (1)$$

where $V$ is the reactor volume, $W$ the rate of desorption, $p$ the pressure of the given component of the gas mixture, and $s$ the rate of evaucation. Each term of Eqn.(1) is usually expressed in litre.mmHg $s^{-1}$, from which values of the rate of desorption expressed in molecule $s^{-1}$ can readily be obtained. If $V(dp/dt) \ll ps$, it follows that

$$W = ps \qquad (2)$$

In the chromatographic version of TD and TPSR, the material-balance equation in the absence of re-adsorption has the form:

$$W = Fc \qquad (3)$$

where $F$ is the velocity of the stream of carrier gas, and $c$ the concentration of the desorbed substance in the carrier gas. Eqns.(2) and (3) have similar forms, and make it possible, by measuring the pressure of the gas above the specimen or the concentration of the desorbed substance in the carrier-gas stream during the TPSR, to determine directly the time (temperature) dependence of the rate of removal of substance from catalyst surfaces into the gas phase.

A term describing the rate of re-adsorption is often included in Eqns.(2) and (3). In a number of cases, allowance for the rate of re-adsorption is necessary,[7] but this complicates the kinetic equations considerably and makes it necessary to study the adsorption separately, so that it is practically impossible to analyse the equations obtained. It is therefore usually preferred to create experimental conditions under which re-adsorption can be neglected, and the rate of desorption can be determined from Eqns.(2) and (3). A sufficiently correct analysis of the influence of re-adsorption on the form of the TD curves has been published.[3,5,8]

As already noted, the products can be analysed chromatographically or mass-spectrometrically. In the first case the desorption products are directed together with the stream of carrier gas into a thermal-conductivity or flame-ionisation detector, and the time (temperature) dependence of the concentration of the product is recorded, that is the TD peak is obtained directly. This method is simple and sufficiently reliable if only one reaction product is liberated. Otherwise, the chromatographic analysis of each substance is necessary, and a series of several peaks, or, as it is usually described, a TPSR spectrum, is obtained. When peaks overlap (when different substances are liberated simultaneously), the problem is complicated, and it is very difficult to obtain TD peaks for each substance separately, even by successive sampling of the products, for example by freezing before chromatographic analysis.

Continuous mass-spectrometric analysis of the gas phase makes it possible to avoid these difficulties, since the change in the concentration of each substance can be followed. The mass spectrometers used for this purpose must satisfy a number of requirements, however. Firstly, the range of masses recorded should cover all the substances studied, including that with the highest molecular mass. It is also necessary to be able to vary the ionising voltage, in order, for example, to reduce as far as possible the extent of the fragmentation of the molecules in the mass spectrometer and hence facilitate the interpretation of the mass spectra obtained. Secondly, the time taken to record the entire mass spectrum should be so short (usually 0.1–1 s) that it is possible to obtain the complete spectrum at the same catalyst temperature. Experience has shown that these requirements are most fully satisfied by quadrupole, monopolar, and time-of-flight mass spectrometers (of the instruments produced in the USSR, the MKh-7304 and MSKh mass spectrometers). It is particularly convenient to use mass spectrometers in which it is possible to record continuously several fixed masses in the computer memory, so that the TD curves for each substance can subsequently be constructed separately.

No special requirements have to be satisfied by the reaction cell in which the catalyst specimen is placed. It is necessary only to note that the volume of the cell should be such that the quantity of catalyst, on the one hand, corresponds to the sensitivity of the recording system, and on the other hand is the minimum quantity, to avoid re-adsorption. The temperature of the specimen is usually measured by a thermocouple placed in the layer of catalyst. It is first necessary to be sure that there are no radial and axial temperature gradients; at the heating rates usually employed ($b$ = 0.01–1 K $s^{-1}$), these effects are insignificant.

## 2. Methods for Determining the Kinetic Parameters of TD and TPSR

One of the problems in TD and TPSR is the determination of the kinetic parameters of the processes of desorption and the surface reaction respectively. In spite of the variety of methods for determining these parameters, they are all based on the Polanyi–Wigner equation

$$W = -dN/dt = kN^n \exp(-E/RT) \qquad (4)$$

where $W$ is the rate of desorption (or of the surface reaction accompanying desorption), $k$ the pre-exponential factor, $N$ the concentration of adsorbed substance, $n$ the kinetic order of the process, $E$ the activation energy, and $T$ the temperature of the catalyst surface.

One method for determining $k$ and $E$ is the so-called linearisation of the thermal desorption curve. In this case, Eqn.(4) and the experimental data (see Fig. 1*b*) are used to construct the plot of $\ln(W/N)$ against $1/T$ or of $\ln(W/N^2)$ against $1/T$ (for processes of first or second order respectively). The concentration ($N$) of the substance remaining on the surface at each temperature is determined as the fraction of the area under the TD curve bounded on the left-hand side by the corresponding temperature (as an example, Fig. 1*b* gives $N_1$ and $N_2$ for temperatures $T_1$ and $T_2$). The slope of the straight line on Arrhenius coordinates gives the activation energy of the process. For this it is sufficient to know the relative values of the rates of liberation of the substance into the gas phase and the degrees of covering ($N$). To determine the pre-exponential factors by this method, however, it is necessary to have data on the absolute values of the rates.

Since in TD and TPSR experiments both the temperature and the degree of covering change continuously, the usual methods for determining the order of the reaction, for example from the dependence of the rate of the process on concentration (in this case the degree of covering) are not applicable, and the order is found from the best agreement

with experimental data from the $\ln(W/N)-1/T$ or $\ln(W/N^2)-1/T$ plots.

If the catalyst is heated by a linear programme ($T = a + bt$) and account is taken of the fact that at the maximum of the TD peak at $T_m$ (see Fig.1*b*) $dW/dT = 0$, then Eqn.(4) gives:

$$E/RT_m = \ln\frac{knN^{n-1}T_m}{b} - \ln(E/RT_m) \qquad (5)$$

or, in slightly modified form, for a process taking place, for example, according to first order kinetics:

$$2\ln T_m - \ln b = E/RT_m + \ln(E/kR) \qquad (6)$$

Eqn.(6) was first proposed by Amenomiya and Cvetanovic.[3] It can be seen from Eqns.(5) and (6) that $T_m$ for the TPSR peak depends on the heating rate. If the dependence of $(2\ln T_m - \ln b)$ on $1/T_m$ is determined experimentally, Eqn.(6) can be used to find the parameters $k$ and $E$ being sought. This method has been called the "displacement of the temperature of the maximum with change in the heating rate" method or the method of Amenomiya and Cvetanovic. Here it should be noted that the experiments must be carried out at constant original degrees of covering of the surface, since otherwise $T_m$ may change even for a constant heating rate. Thus Eqn.(5) and Fig.2 show that it is only for a first-order process that $T_m$ is independent of the degree of covering of the surface, and that for a second-order reaction, $T_m$ decreases, and for a zeroth-order reaction $T_m$ increases, with increase in the original concentration of the adsorbate. For second-order processes, the form of the TD peak is symmetrical.

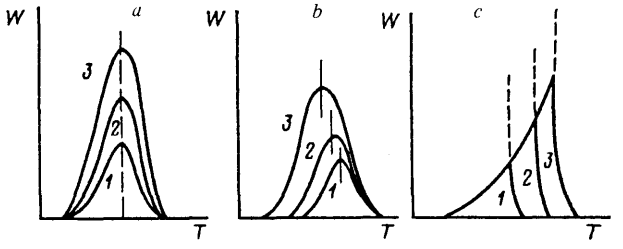



Figure 2. Schematic representation of the TD curves for processes of first (*a*), second (*b*), and zeroth (*c*) orders; the original coverage increases from (*1*) to (*3*).

To determine the kinetic parameters of desorption and surface reactions, extensive use has been made of a method based on the measurement of the so-called half-width of the TD peak $\Delta T = T_2 - T_1$, that is the difference between the temperatures at which the rate of the process is equal to half the maximum rate (see Fig.1*b*).[9,10] According to Eqn. (4), the expressions for the rates of the process at $T_1$ and $T_2$ can be written in the form:

$$\frac{W_m}{2} = kN_1^n \exp(-E/RT_1); \quad \frac{W_m}{2} = kN_2^n \exp(-E/RT_2) \qquad (7)$$

which gives:

$$E = \frac{R\ln(N_1/N_2)^n T_1T_2}{\Delta T} . \qquad (8)$$

Eqn.(8) shows that the factor $T_1T_2/\Delta T$ is independent of the heating rate. It is therefore possible to determine the activation energy from one experiment. Computer calculations by the present author showed that the first-order processes, $\ln(N_1/N_2)$ is constant, and that for second-order processes, $\ln(N_1/N_2)^2$ changes little, even with change in the concentration by a factor of 10. Using the calculated values of these parameters, the expressions for the activation energies of the first- and second-order processes can be written in the form:

$$E = 4.6T_1T_2/\Delta T \text{ for } n = 1;\ E = 6.2T_1T_2/\Delta T \text{ for } n = 2. \qquad (9)$$

The order of the reaction can be estimated from the form of the peak (see Fig.2). A more accurate equation for calculating $E$ for second-order processes using the half-widths of the TD peaks has been proposed.[11] The pre-exponential factors can be calculated (if the value of $E$ is known) using Eqns.(4) and (5) or a simplified form of Eqn.(5).[9]

The method in which $E$ is determined using the parameter $\Delta T$ and hence Eqn.(9) or the published equations[11] is much less sensitive to various experimental errors than the method based on the measurement of the dependence of $T_m$ on the heating rate.

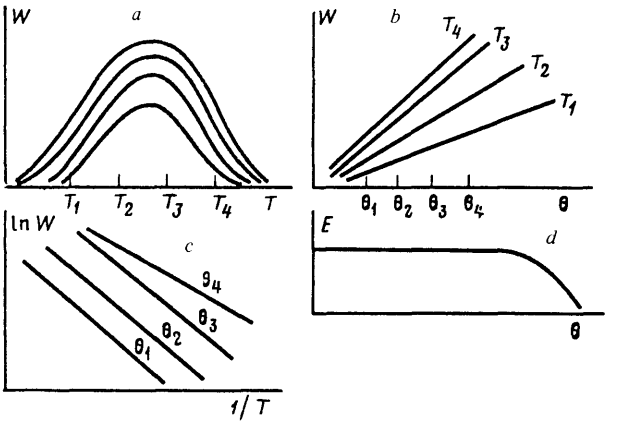



Figure 3. The method of "desorption isotherms": *a*) family of desorption curves for different original degrees of covering, *b*) desorption isotherms, *c*) Arrhenius relationships for constant degrees of covering, *d*) dependence of $E$ on the degree of covering.

The above methods for determining the kinetic parameters are applicable to the analysis of individual TD or TPSR peaks reflecting processes taking place on uniform surfaces. For the analysis of processes taking place on non-uniform surfaces, the so-called method of "desorption isotherms" has been proposed.[12,13] It is based on a series of thermal desorption experiments differing in the original degree of covering of the surface. The original data in this case can be represented in the form of a family of curves (this method is illustrated in Fig.3), each point of which corresponds to a definite rate of the process, temperature, and degree of covering of the surface $\theta$. These data are used to construct desorption isotherms (Fig.3*b*), that is the dependence of $W_{des}$ on $\theta$ (or $N$) for several constant temperatures. These relationships make it possible to determine the order of the process if the data are represented, for example, on coordinates $\ln W - \ln\theta$ (in Fig.3*b* the order of the reaction is 1).

The Arrhenius relationships are then constructed for a series of constant values of the degree of covering (Fig.3c), and finally the dependence of the activation energy on the degree of covering is calculated (Fig.3d). The great advantage of this method is that in the treatment of the data it is not necessary to know beforehand or to assume the kinetic order of the process. Moreover, the form of the $E = f(\theta)$ relationship shows clearly whether the surface is uniform or non-uniform.

Later, it was suggested that the heating rate be varied instead of the initial degree of covering;[14] this makes it possible to cover a wider temperature range for the process, and hence to calculate its kinetic parameters more accurately. It has been pointed out,[15] however, that if both $E$ and $k$ depend on the degree of covering, the dependence of the rate of the process on the concentration of adsorbed substance (Fig.3b) may not reflect the true order of the reaction.

In addition to the above methods for determining the order of the reaction, mention must be made of another method, based on the analysis of the shape of the TD or TPSR peaks. It has been proposed[16] that the order of the desorption be estimated using the so-called "shape index" $S$, which is the ratio of the slopes of the tangents to the TD peak at the points of inflection on the ascending and descending branches. The values of this parameter were subsequently calculated[8] for four cases: for first- and second-order desorption processes with and without re-adsorption. These calculations[8] were subsequently refined.[17] Here, however, it may be noted that according to the published data,[8] the parameters $S$ for first- and second-order processes in the absence of re-adsorption have different values and are independent of the original degree of covering. At the same time, the values of $S$ are similar for first-order desorption without re-adsorption and for second-order desorption with re-adsorption. This situation makes it difficult to determine the kinetic order of the process; moreover, since graphical differentiation of the TD (or TPSR) peak is necessary, the uncertainty of the determination of the parameter $S$ is high.

The kinetic parameters of the desorption or the surface reaction can be determined using appropriate mathematical programs which make it possible to select these parameters on the basis of a regression analysis to give best agreement with the experimental curve. This method can be used even for overlapping peaks,[18] although it is pointed out[18] that it is difficult to choose between different models. An undoubted advantage of this method is that it is possible to vary the dependence of $k$ and $E$ on the degree of covering; this was clearly demonstrated[19] in an analysis of the experimental TD spectra for but-1-ene from the surface of NaY zeolites.

The principal methods of determining the kinetic parameters of desorption have been examined. The most suitable methods for the treatment of single peaks are apparently the half-width method and the linearisation of the TD curves on Arrhenius coordinates. These methods are simple and sufficiently reliable. If the peaks overlap or if there is extensive non-uniformity of the surface, however, the method of "desorption isotherms" is preferred. Naturally, all the above methods for determining the kinetic parameters of thermal desorption are also applicable when chemical transformations take place on the surface. In this case the kinetic parameters obtained from the curves giving the time (temperature) dependence of the removal of the reaction products reflect both their desorption into the gas phase and the processes taking place on the catalyst surface. Moreover, the TPSR method makes it possible, in particular, to obtain information on the presence of active centres of different types, stepwise mechanisms, the limiting stage of the process, and intermediate compounds.

## III. REACTIONS ON CATALYST SURFACES

### 1. Active Centres of Different Types

In ordinary thermal desorption, when the interaction of the gas with the surface takes place without change in the chemical composition of the particles, the existence of adsorption centres of different types is indicated by the existence of several TD peaks. Similarly, in TPSR, the appearance of several peaks for the same reaction product may indicate non-uniformity of the active surface in the given reaction. In this case, however, there may be several factors responsible for this type of TPSR spectrum, so that additional experiments are required to prove the existence of active centres of different types. This is particularly necessary in the case of deposited catalysts.

Thus if it is assumed that there is only one type of centre on which the reaction takes place, but that the carrier contains pores with different dimensions, then in this case, even if the reaction takes place with the same rate constant on all the active centres, the removal of the products into the reaction space free from catalyst (where the concentration is properly measured) may be determined by the rate of diffusion from different pores and by re-adsorption. Thus the existence of several peaks will indicate not the existence of active centres of different types but a distribution of the pore sizes in the carrier. It is therefore first necessary to estimate the rates of diffusion and adsorption and to be satisfied that these processes do not influence the nature of the TPSR spectrum (the positions and half-widths of the peaks). This can be done experimentally by varying the particle size of the catalyst, the weight of catalyst, and the rate of evacuation (or the velocity of the stream of carrier gas), and hence changing the concentration of the reaction product over the catalyst.

A second and apparently more significant factor responsible for the existence of several peaks for a given product is related to the kinetic characteristics of the reaction. If it is assumed that the reaction on the surface takes place according to the simple scheme A → B → C → D, and if the adsorption of the compound A is carried out at a sufficiently high temperature, then at the start of the actual TPSR experiment the reaction may already have taken place to some extent, and the compounds A, B, and C may be present on the surface in definite concentrations. In this case, when the catalyst is heated, the appearance of the product D in the gas phase will be determined by the rate constants of three corresponding processes, namely A → B → C → D, B → C → D, and C → D, and this may lead to the appearance of several peaks for the product D in the TPSR spectrum. To determine whether this effect is present, it is necessary to carry out the adsorption at different, preferably lower, temperatures. In this case the transformation of the adsorbed substance A into B and C will naturally be hindered, and in the limiting case, only the substance A will be present on the surface at the start of the TPSR experiment. If change in the adsorption temperature does not lead to a decrease in the number of peaks for the product, this indicates that active centres of different types are in fact present on the surface.

Another method for proving the presence of different centres on a catalyst surface is by modifying the centres in some way and then analysing the TPSR spectra. This approach has been used, in particular, in a study[20] of the dehydrocyclisation of n-heptane on deposited platinum specimens with different degrees of dispersion (Fig.4). Fig.4 shows that there is a correlation between the intensity of the high-temperature peak of toluene and the degree of

dispersion of platinum. Thus the TPSR spectrum in this case does in fact characterise the catalyst. This spectrum can be used to determine the kinetic parameters of the process on centres of each type, and their concentration. Thus the TPSR method, in addition to providing a means of investigating the mechanism and kinetics of the reaction being studied, also makes it possible to characterise the catalyst itself.

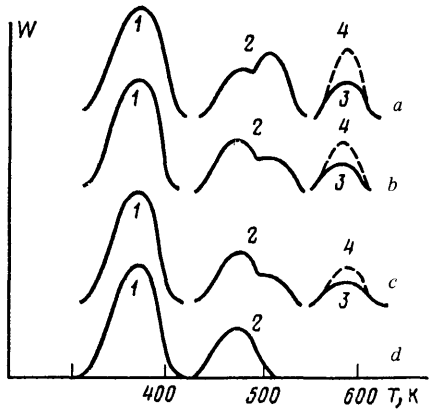



Figure 4. TPSR spectra of n-heptane on $Pt/Al_2O_3$ specimens with different platinum particle sizes, Å: *a*) 13, *b*) 17, *c*) 38, *d*) 1000; *1*) heptane, *2*) toluene, *3*) benzene, *4*) methane.[20]

## 2. Stepwise Mechanisms of the Surface Reaction and the Limiting Stage

The advantages of the TPSR method are possibly revealed to the greatest extent in the study of the mechanisms of catalytic reactions. Although such reactions as the recombination-desorption of diatomic molecules naturally are also surface reactions, the application of the TPSR method to more complex processes such as catalytic decomposition, oxidation, dehydrogenation, and dehydrocyclisation will be considered.

A study of the decomposition of hydrazine and ammonia on $Ir/Al_2O_3$ by the TPSR method and infrared spectroscopy[21] showed that the reaction of hydrazine with the catalyst surface leads to the appearance, in addition to the peaks of the main products, of an additional peak due to nitrogen remaining in the adsorbed state in the atomic form up to high temperatures. The high strength of the bond formed by the nitrogen atoms with the surface was regarded[22] as the factor responsible for the gradual decrease in the activity of the $Ir/Al_2O_3$ catalyst during the decomposition of $N_2H_4$ when the process was carried out under stationary conditions. As in the earlier studies,[21] a single nitrogen peak with $T_m \cong 670$ K was observed, whereas the formation of $NH_3$ takes place chiefly in the temperature range 300–500 K (Fig.5). The appearance of the nitrogen peak with $T_m = 670$ K in the decomposition of both $N_2H_4$ and $NH_3$ indicated[22] that the reaction of $N_2H_4$ with $Ir/Al_2O_3$ leads to rupture of the N–N bond in the hydrazine molecule.

Even this TPSR study[22] essentially used a procedure involving the preliminary adsorption of possible intermediate compounds (in this case $NH_3$, which is readily transformed into $NH_2$). This approach was apparently used in most complete form in studies[23,24] which showed that the principal route in the dehydrocyclisation of $C_6$–$C_7$ hydrocarbons on $Pt/Al_2O_3$ involves the stepwise dehydrogenation of the starting material.

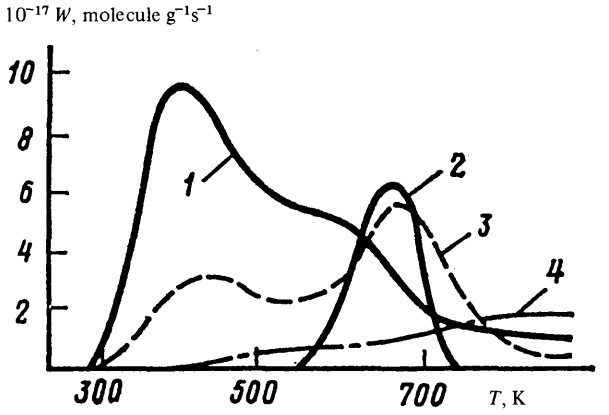



Figure 5. TPSR spectra of $N_2H_4$ on 0.38% $Ir/Al_2O_3$ (complete covering by $N_2H_4$ at 298 K); *1*) $NH_3$ (rate *W* increased by a factor of 1.3), *2*) $N_2$ (×2.1), *3*) $H_2$, *4*) $H_2O$ (×25).[22]

This approach can be examined in slightly more detail. If it is assumed that the reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} C_{gas}$ takes place on the surface and that the limiting stage is the transformation of B into C, then the parameters determined from the peak for the liberation of C into the gas phase should coincide for the adsorption of the substances A or B, but after the adsorption of the substance C the $C_{gas}$ peak should be displaced to lower temperatures. On the other hand, this approach makes it possible to determine the limiting stage of the process. On the other hand, if the rate constants for the formation of $C_{gas}$ from A and from B, determined by the TPSR method, coincide completely, this indicates that B is in fact an intermediate compound in the chain of successive transformations of A into $C_{gas}$.

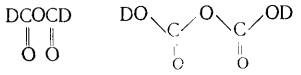
Using this approach, it has been possible to show[23] that the dehydrogenation of cyclohexane on platinum catalysts takes place on centres of two types, corresponding to two benzene peaks (Fig.6). The limiting stage on centres of one type is the transformation of cyclohexane into cyclohexene, and that on the centres of the other type is the desorption of the firmly bound form of benzene.

The question naturally arises of whether the suggested intermediate substances in adsorption give the same surface forms as are produced during the reaction. It is difficult to answer this question unambiguously, and its solution requires the use of other independent methods, for example spectroscopy.

To investigate the reaction mechanism it is important to carry out a complete analysis of the thermal-desorption curves for all the reaction products. A detailed study carried out in this way made it possible[25] not only to determine the mechanism of the decomposition of methanol on pure tungsten but also to follow the change in the mechanism of this reaction as carbon was deposited on the catalyst surface. Other similar examples have been described.[26–29]

In particular, in a study of the decomposition of labelled formic acid DCOOH on a single crystal of nickel,[29] it was

shown (Fig.7) that the decomposition products $D_2$ and $CO_2$ are desorbed simultaneously at $T_m$ = 400 K, and that CO is desorbed at higher temperatures (the narrow CO peak in Fig.7 corresponds to a mass-spectrometric fragment of $CO_2$). The study of the adsorption of carbon monoxide itself showed that CO is desorbed at the same temperatures as the CO obtained by the decomposition of formic acid. The simultaneous removal of $CO_2$ and $D_2$ indicates that the desorption of these products is not the limiting stage (otherwise they would have different $T_m$). Quantitative analysis showed that $D_2$, $CO_2$, and CO are liberated in the ratio 1 : 1 : 1. Since $H_2O$ was formed and liberated at much lower temperatures, the following two possible forms were proposed for the adsorbed intermediate, from which the products indicated are obtained:



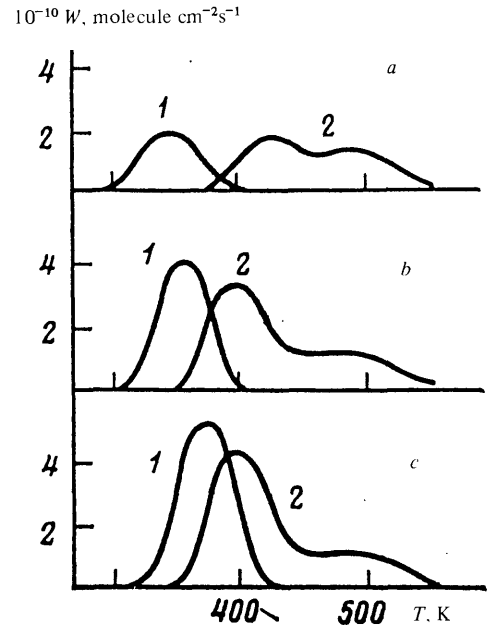




Figure 6. TPSR spectra after the adsorption of cyclohexane (*a*), cyclohexene (*b*), and cyclohexadiene (*c*) on $Pt/Al_2O_3$: *1*) original hydrocarbon, *2*) benzene.[23]

Labelled molecules were used in this study,[29] although attention was not concentrated on the distribution of isotopes in the reaction products. This approach, however, can give valuable information on the surface process. In a study of the oxidation of ethanol on a single crystal of silver,[29] $^{18}O_2$ and $CH_3CH_2OD$ were used to distinguish the hydrogen joined to hydrogen atoms from the hydrogen in the hydroxyl group. $D_2O$, $H_2$, $C_2H_4$, $CH_3CH_2OH$, and $CH_3CH_2O$ were detected in the reaction products. The TPSR spectra obtained, and the distribution of the isotopes in the reaction products, led to the following conclusions: 1) on adsorption, the hydroxyl group of the alcohol reacts with the surface $^{18}O$ atoms to give adsorbed $CH_3CH_2O$ and $D_2O$; 2) the simultaneous appearance of $CH_3CH_2OH$, $CH_3CHO$, and $H_2$ in the gas phase indicates that all these products are formed from the same intermediate, namely the adsorbed species $CH_3CH_2O$; and 3) the formation of $C_2H_2$, $D_2^{16}O$, and $H_2$ from $CH_3CH_2^{16}OD$ is associated with the decomposition of a surface complex consisting of two alcohol molecules.

An analysis[30] of the liberation of $D_2$ and deuteriated derivatives of benzene during the dehydrogenation of cyclohexane ($C_6D_{12}$ was used to distinguish the hydrogen liberated from the cyclohexane molecule from the hydrogen adsorbed during the reduction of the catalyst) confirmed the earlier conclusion[23] that this process takes place on centres of two types. On the low-temperature centres the process is limited by the removal of hydrogen, whereas on the high-temperature centres the slowest stage is the addition of surface hydrogen to the dehydrogenated form of benzene.

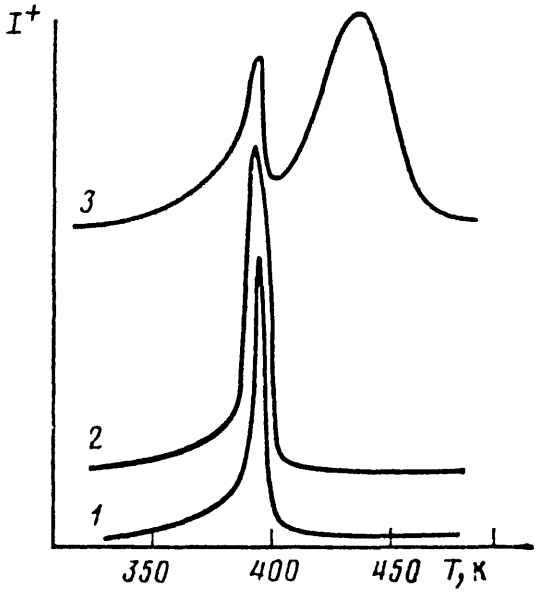
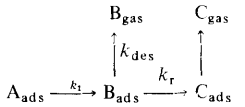



Figure 7. TPSR spectra after the adsorption of DCOOH on Ni(110) at 310 K: *1*) $D_2$, *2*) $CO_2$, *3*) CO; $I^+$ is the mass spectrometer signal.[29]

## IV. INTERMEDIATE REACTION PRODUCTS

In the great majority of cases, the intermediate products of the surface reactions are liberated into the gas phase in such small quantities that they cannot be detected by ordinary methods. This is due to the fact that the rate constant of the surface process is generally appreciably greater than the rate constant of the desorption of the intermediate substance. It has been shown,[31-33] however, that if the catalyst surface is heated very rapidly, it becomes possible to observe the intermediate and final reaction products simultaneously. Thus if for example the following transformations take place on the surface




and that the limiting stage is $A_{ads} \rightarrow B_{ads}$, then the liberation of the products $B_{gas}$ and $C_{gas}$ will be determined by the constant $k_1$. In this case they will appear almost simultaneously, and

the heating rate will have little influence on their relative quantities. If however the surface process is limited by the stage $B_{ads} \rightarrow C_{ads}$, then in this case the relative integral yield of the product $B_{gas}$ will increase sharply with increase in the heating rate. An example is provided in Fig. 8, which gives the dependence of the yield of the intermediate substance on the heating rate for various typical parameters of the separate stages.

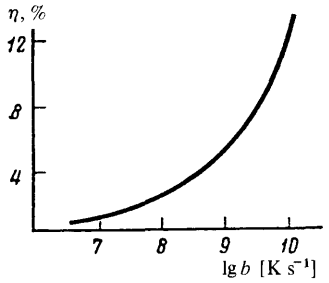



Figure 8. Dependence of the yield of intermediate substance $\eta$ on the heating rate $b$ at $E_{des}$ = 63 kJ mole$^{-1}$, $E_r$ = 42 kJ mole$^{-1}$, and $k^0_{des}/k^0_r = 10$.[33]

It has been suggested[31,32] that pulse laser sources be used to obtain high heating rates ($b > 10^4$–$10^5$ K s$^{-1}$). Because of the finite dimensions of the space of the drift of the desorbed species from the surface being studied to the analyser, the time resolution of the recording systems (mass spectrometers) was worse than $10^{-4}$–$10^{-5}$ s, that is the traditional TD or TPSR curves could not be obtained, and the mass-spectrometric analysis made it possible to determine only the integral yield of products. The approach developed in Ref. 33 made it possible to propose a method for determining the kinetic parameters of the desorption of intermediate products, based on the measurement of their integral yields at different heating rates.

Laser-stimulated thermal desorption has been used[34] to detect the intermediate products of the dehydrocyclisation of alkanes. It was shown that in the case of hexane, the reaction involves the intermediate formation of hex-2-ene and hexadiene. The same method has been used[35,36] to study the reaction of acetaldehyde with copper oxide catalysts. The change in the predominant direction of the transformations of the adsorbed species with change in the rate of heating of the catalyst was demonstrated for the decomposition of methanol on a nickel surface.[37] It was shown[37] that during slow TPSR ($b \cong 7$ K s$^{-1}$), less than 10% of the original methanol is liberated into the gas phase (in this case it must be regarded as an intermediate product), and the rest is in the form of $H_2$ and CO. In the case of laser TPSR, however, the opposite picture is observed, that is the chief product after the adsorption of methanol at low temperatures is $CH_3OH$.

The use of pulse lasers with a high quantum flux density per unit surface area can in principle lead to effective decomposition of the species on the surface. To verify this it is necessary to carry out additional experiments, as for example in a comparison[34] of the effect of laser radiation on hexane adsorbed on a $Pt/Al_2O_3$ catalyst and on the $Al_2O_3$ carrier. The decomposition of hexane was slight in both cases, but the liberation of reaction products, namely benzene, hexene, and hexadiene, was observed only in the experiments with $Pt/Al_2O_3$. These data indicate that a catalytic process is taking place, and that there are no chemical transformations of the molecules in the gas phase directly under the influence of the laser radiation.

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The material reviewed showed that the TPSR method can be used to determine the kinetic parameters of a surface process and its limiting stage, to reveal non-uniformity of catalyst surfaces, and in a whole series of cases to establish the reaction mechanisms. Additional information can be obtained by combining the TPSR method with, for example, infrared spectroscopy or other methods for studying surfaces.† It is always necessary, however, to take account of a characteristic feature of TPSR, namely the absence of the original compounds from the gas phase. Thus when transferring data obtained by the TPSR method to ordinary catalysis, care is required, and it is necessary in every case to be satisfied that the introduction of the original substances into the gas phase does not change the reaction mechanism.

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# The Chemisorption of Oxygen and the Oxidation of Carbon Monoxide on Metals

V.I.Savchenko

Data on the chemisorption of oxygen on a number of metals (Pt, Pd, Ir, Ru, Ni, etc.), obtained by SED, EAS, XES, etc., have been reviewed. The bond energies and principal properties of the two types of $O_{ads}$ on metals (non-reconstructive and reconstructive), and also the conditions for the realisation of each type of adsorption, have been examined.
The bibliography contains 84 references.

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## I. INTRODUCTION

The nature of the chemisorption compounds, the energy of the bonds formed, and hence the mechanism and kinetics of the reactions depend on the chemical composition and structure of the metal surface. Many authors[1-3] have noted a similarity between the properties of chemisorption compounds and complex compounds or oxides, carbides, and nitrides. For example, in the chemisorption of oxygen, a whole series of compounds may be formed, from molecular forms to three-dimensional oxides. The heats of adsorption of the molecular forms $O_{2ads}$ are 40–50 kJ mole$^{-1}$; their desorption temperature is low, $T_{des}$ = 120–150 K; and the reactivity of $O_{2ads}$ is low.[4] The forms of greatest interest for catalysis on metals are adsorbed atomic forms of oxygen at degrees of covering less than a monolayer, which are present on the surface at the temperatures of "real" catalysis (300–800 K).

One of the most important questions is whether the chemisorption of oxygen atoms takes place on the surface or whether they are inserted into the surface layer, with a simultaneous displacement of the metal atoms. The possibility of adsorption in the non-reconstructive (type I) or reconstructive (corrosion) (type II) forms was examined in Ref.1. Subsequently, as a result of the development of physical methods for studying surfaces (slow electron diffraction (SED), electronic Auger spectroscopy (EAS), X-ray electron spectroscopy (XES), thermal desorption (TD), low-energy electron characteristic loss spectroscopy, etc.), this question was discussed by a large number of authors. As emphasised by Boreskov,[5] "in a solid catalyst–reactant system, transformations are undergone not only by the reactants under the influence of the catalyst, but also by the catalyst as a result of chemical interaction with the reactants". The reaction medium will obviously have a greater effect on the catalyst when at least one of the reactants under the reaction conditions is chemisorbed in the reconstructive form (type II). Thus the phenomena of catalytic corrosion have been related to reconstructive adsorption.[6] The nature of the chemisorption (type I or II) apparently influences the reactivity of the species and the form of the kinetic relationships describing the adsorption and the catalytic reaction.

The present review examines data on the influence of the nature and structure of the surface on the state of adsorbed oxygen species and the oxidation of CO on a number of metals (Pt, Pd, Ir, Ru, Ni), obtained by SED, TD, and electron spectroscopy.

On all the above metals, carbon monoxide is adsorbed in molecular forms (linear and bridged) with approximately identical heats of adsorption $\Delta H$ between −100 kJ mole$^{-1}$ and −150 kJ mole$^{-1}$; the influence of the structure of the surface is even stronger than the influence of the nature of the metal. The bond between CO and the metals is a donor–acceptor bond. Photoelectron spectroscopy (PES) has shown[7,8] that the $CO_{ads}$ molecules are joined to the metal through the carbon atom and are arranged at right angles to the surface.

On the other hand, the energies of the bonds formed by oxygen with the above metals vary from 180–220 kJ mole$^{-1}$ (Pt) to 500 kJ mole$^{-1}$ (Ni). This indicates that a decisive role in the change in the catalytic activity in this series of metals is played by the change in the bond energy and state of the adsorbed oxygen. In the present review, therefore, particular attention is paid to the chemisorption of oxygen on metals.

## II. MECHANISM OF THE ADSORPTION OF OXYGEN ON METALS

When oxygen is chemisorbed on the surface of metal single crystals, the $O_{ads}$ atoms are not arranged randomly, but form definite structures. The diffraction patterns obtained by SED may result from the scattering of electrons on ordered oxygen atoms on the surface (adsorption of type I) or on metal atoms which have undergone ordered displacements on reconstructive (corrosion) chemisorption (adsorption of type II). It can also be said that in chemisorption of type II, surface oxides are formed, since a mixed layer consisting of oxygen and metal atoms is produced.

In the nineteen-sixties, on the basis of the concept of the once-only scattering of electrons (the kinematic theory of diffraction), it was concluded[9] that the adsorption of oxygen on nickel is reconstructive, for example, it was assumed that in the structure Ni(100)–c(2 × 2)O, every second nickel atom is replaced by an oxygen atom. Later calculations[10] carried out in accordance with the complete program of the dynamic theory of diffraction, that is with allowance for multiple scattering of the electrons, led to a model of the adsorption of type I in which the oxygen atoms are situated at a distance of 0.9 Å above the metal. This adsorption scheme, however, is not consistent with the data obtained by other methods, for example ion-neutralisation spectroscopy.[11] Thus in Ref.12

it was noted that the c(2 × 2)O structure can probably be produced in adsorption of both type I and type II.

Criteria for establishing the type of adsorption may be provided by the following data: 1) the change in the work function: $\Delta\phi \cong 0.5-1.0$ eV for adsorption of type I, and $\Delta\phi < 0$ eV for adsorption of type II; 2) the form of the EAS spectrum, namely the change in the ratio of the peaks in the Auger spectrum of oxygen. Thus the Auger spectrum of oxygen in the Ni(111)–(2 × 2)O structure practically consists of two peaks, whereas for reconstructive chemisorption and for oxygen in nickel oxide, the Auger spectrum shows three peaks: $KL_1L_1$, $KL_1L_2$, and $KL_2L_2$; 3) the temperature dependence of the intensity of additonal reflections. For reconstructive adsorption, this relationship approximately coincides with the temperature dependence of the principal reflections, for example for the structure W(100)–(2 × 1)O, whereas for non-reconstructive adsorption in the (4 × 1)O structure there is a sharp decrease in intensity with increase in temperature, due to the production of disorder in the adsorption layer.[13]

## 1. The Chemisorption of Oxygen on Pt, Pd, Ir, Ru, and Ni

### *a) Adsorption on nickel*

According to EAS data, the kinetic curve for the adsorption of $O_2$ on the (111), (110), and (100) faces of Ni at 300 K consists of two main regions:[14,15] the first corresponds to rapid chemisorption, and the second is associated with the nucleation of isolated regions of the phase NiO (induction period) and the subsequent growth of the isolated regions to form a continuous NiO film with a thickness of 2–3 monolayers.

A detailed study of the kinetics of the chemisorption of $O_2$ at a low pressure ($p(O_2) = 2 \times 10^{-7}$ Pa) on Ni(100) at 433 K showed[15] that after the p(2 × 2)O structure is completely filled with oxygen; a slight induction period is observed, followed by an increase in the rate of chemisorption with the growth of the isolated regions of the c(2 × 2)O structure. The topochemical character of the kinetics of the chemisorption with the formation of the c(2 × 2)O structure, analogous to the kinetics of the formation of NiO, indicates that the adsorption in this case is reconstructive, that is a two-dimensional oxide is formed. To investigate the nature of the adsorption when the Ni(100)–c(2 × 2)O structure is formed, oxygen was adsorbed at 170 K to a degree of covering $\theta = 0.5$.[16] A structure was not formed, but the work function increased by 0.5 eV. Next, the crystal was stepwise heated to 600 K. Formation of the c(2 × 2)O structure at 250–300 K was accompanied by a decrease of the work function by 0.3 eV in comparison with that of a clean Ni(100) surface. It may be noted that the "order–disorder" transformation in layers of type I does not lead to a change in the work function. This was shown in analogous experiments[17] for the non-reconstructive adsorption of oxygen on an Ru(0001) face. Thus the decrease in the work function when the Ni(100)–c(2 × 2)O structure is formed must be due to the insertion of $O_{ads}$ into the lattice, that is to the formation of a layer of type II.

It was found qualitatively (visual estimation) that there is no significant decrease in the intensity of the SED pattern on p(2 × 2)O and c(2 × 2)O when the crystal is heated to 700 K. It was recently found[18] that disorder is produced in the Ni(100)–c(2 × 2)O structure only at 900 K, and that simultaneously, judging from the EAS data, oxygen disappears from the surface, that is the production of disorder in the layers of this type is due to the breakdown of the lattice (2D) of the oxide and the solution of oxygen in the bulk of the metal.

Quantum-chemical calculations by the generalised valence bond method[19] led to the conclusion that two states of oxygen can exist on an Ni(100) surface: in the first, radical-like state ($O^-_{ads}$), the oxygen atom is at a distance $d = 0.9$ Å from the surface (adsorption of type I), and in the second state ($O^{2-}_{ads}$) the oxygen atom of the surface oxide is at distance $d = 0.23$ Å from the surface (adsorption of type II). The oxygen bond energy in state II is 60 kJ mole$^{-1}$ greater than that in state I. State I is possibly produced on Ni(100) at $T \leq 250$ K, and state II in the c(2 × 2)O structure. The change from $O_{ads}$(I) to $O_{ads}$(II) for a given degree of covering ($\theta = 0.5$) leads to appreciable suppression of the adsorption of CO.[20]

When $O_2$ is adsorbed on Ni(110), a succession of structures appears: (3 × 1)O, (2 × 1)O, (3 × 1)O again, p(9 × 4)O, and finally (100)NiO. Their ranges of existence are separated by short induction periods.[21] Ion-scattering spectroscopy showed[22,23] that the Ni(110)–(2 × 1)O structure consists of alternating (at intervals of one) rows of nickel atoms, as suggested in Ref. 9.

Fig. 1 gives a representation of the structural transformations taking place when $O_2$ is adsorbed on Ni(111).[24] The start of adsorption at 300 K gives the (2 × 2)O structure, in which oxygen is probably adsorbed according to type I, since the Auger spectrum differs from that of oxygen in NiO, the work function increases by 0.5 eV on adsorption, and the temperature at which disorder is produced in the layer is 480 K. The production of disorder in the layer is accompanied by the reversible transfer of some of the $O_{ads}$ into the

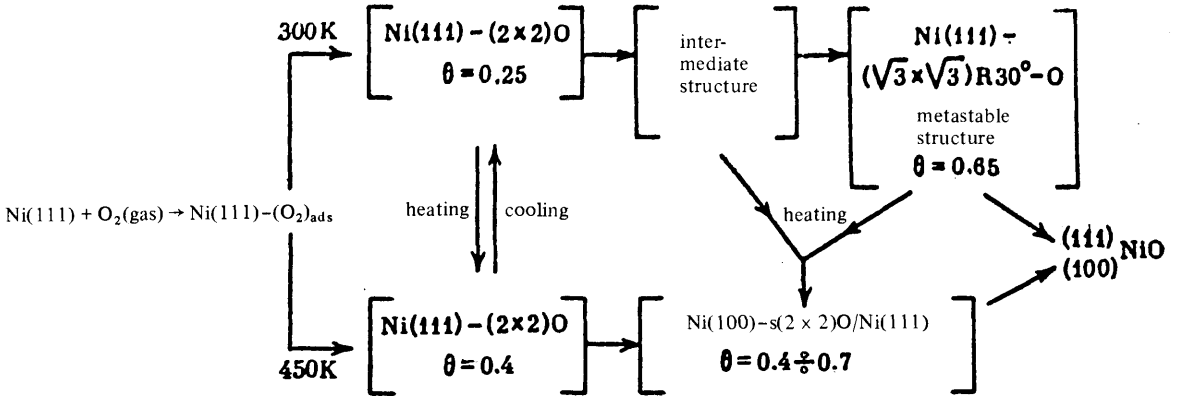



**Figure 1.** Structural transformations when $O_2$ is adsorbed on Ni(111).

surface region. With increase in the degree of covering ($\theta = 0.65$) at 300 K the structure ($\sqrt{3} \times \sqrt{3})R30°$–O appears. This structure is metastable, since on heating to 450 K it is transformed irreversibly into Ni(100)–c(2 × 2)O//Ni(111), that is for adsorption of type II, "reorientation" of the surface oxide into the most favourable configuration is possible, as a result of which the structure of the layer is the same, namely c(2 × 2)O on the (100) and (111) faces. A similar "reorientation" of the Ni(111) face was observed when sulphur is adsorbed.[25]

*b) Adsorption on ruthenium*

Oxygen adsorbed at 300 K on Ru(0001) is desorbed at $T_{des} = 1200–1300$ K; $E_{des}$/kJ mole$^{-1} = 400 - 80\ \theta$.[17,26] EAS has shown, however, that heating even at 400–600 K leads to an irreversible decrease in the magnitude of the Auger peak of oxygen. This can be attributed to the conversion of $O_{ads}(I)$ into the surface-oxide state (adsorption of type II) and the resulting shielding of the oxygen atoms by the ruthenium atoms and increase in the effective charge on the oxygen atom. The equation and kinetic constants were obtained for the transformation $O_{ads}(I) \rightarrow O_{ads}(II)$. The activation energy of this transformation is ~20 kJ mole$^{-1}$. The formation of $O_{ads}(II)$ leads to a decrease in the subsequent adsorption of carbon monoxide in the layer.[26,27]

*c) Adsorption on iridium*

The principal adsorption properties of the (111) and (110) faces of Ir have been described.[28] A clean Ir(110) surface, which has the (1 × 2) structure, after several oxygen adsorption and thermal desorption cycles is rearranged to give a (1 × 3) structure, due to micro-facetting of the surface by (111) faces.[29]

When $O_2$ is adsorbed on Ir(111), a (2 × 2) diffraction pattern is observed, due to the existence of (2 × 1)O domains with three orientations, since $\theta = 0.5$.[30] EAS data and contact potential difference measurements indicate that the adsorption of oxygen on Ir(111) is of type I. The development of the (2 × 2) structure on the Ir(111) face is delayed relative to adsorption, indicating that adsorption takes place on any surface centres, after which ordering of the layer takes place as a result of lateral interaction between the $O_{ads}$ atoms. Calculation of the energy of the lateral interaction from the temperature of the production of disorder in the (2 × 2)O layer ($T_c = 480$ K) in the Bragg–Williams approximation gave the value 4–8 kJ mole$^{-1}$.[30]

At $T \geqslant 450$ K on Ir(110), a non-stoichiometric surface oxide is formed,[14,28,29] and the (110)–(1 × 3) structure is converted into (110)–(1 × 1)O. The activation energy of the transformation is ~80 kJ mole$^{-1}$. As on Ni and Ru, on Ir the transformation $O_{ads}(I) \rightarrow O_{ads}(II)$ leads to a decrease in the heat of adsorption of carbon monoxide (by ~30 kJ mole$^{-1}$ according to Ref. 31).

*d) Adsorption on platinum*

On Pt(111) and on a stepped surface Pt(s), oxygen is adsorbed in the (2 × 2)O structure. In the initial stage on Pt(s), the structure 2(1D)O is formed, that is the atoms are adsorbed on platinum steps with intervals of one atom. The activation energy of desorption $E_{des} = 240 - 50\ \theta$ kJ mole$^{-1}$.[32]

The temperature dependence of the intensity of the (1/2, 1/2) reflections showed (curve *2* in Fig. 2*a*) that complete disordering of the (2 × 2)O layer on Pt(111) takes place even at 420 K.[33] For Pt(s), the graph consists of two regions (curve *3* in Fig. 2*a*): a region corresponding to a sharp decrease in the intensity of the reflections of the (2 × 2)O layer on terraces, similar to curve *2* for Pt(111), and a region corresponding to a relatively weak temperature dependence, associated with "bands" of the 2(1D)O structure, which pass through the positions of the (1/2, 1/2) reflections. Since the oxygen adsorbed on the steps in the 2(1D)O structure does not undergo disordering up to the desorption temperature, the adsorption on the steps is apparently reconstructive (type II).

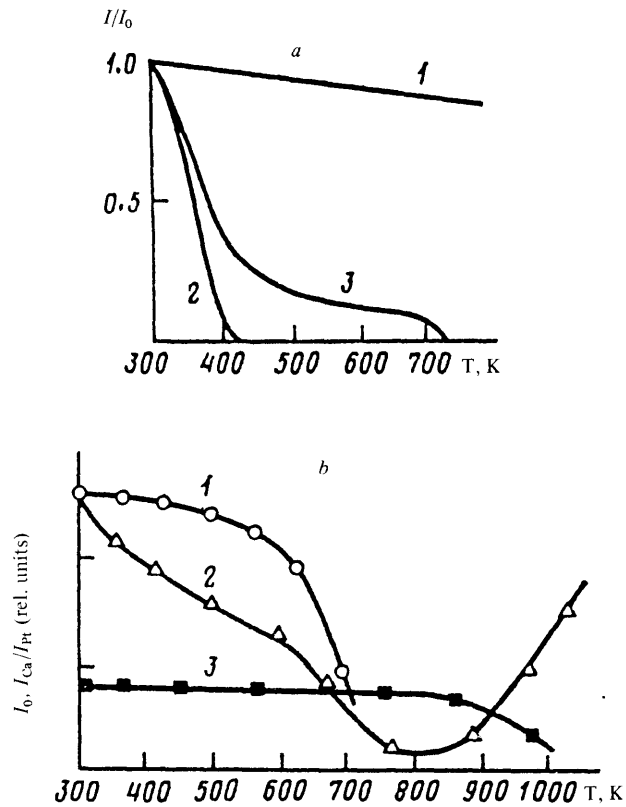



Figure 2. *a*) Temperature dependence of the intensity of the principal (1, 0) (*1*) and additional reflections of a layer of oxygen on Pt(111) (*2*) and Pt(s) (*3*); *b*) change in the magnitude of the Auger peak of oxygen on heating in a vacuum after the adsorption of $O_2$ on Pt at 300 K (*1*) and on heating in a flow of oxygen (*2*), and the temperature dependence of the concentration of calcium (*3*).

EAS has shown[34] (curve *1* in Fig. 2*b*) that when the (2 × 2)O layer on platinum is heated, no appreciable solution of oxygen takes place up to the desorption temperature, in contrast to the case of iridium[29] and rhodium.[35] If however platinum is heated in a stream of $O_2$ (curve *2*), then at high temperatures (800 K) the quantity of oxygen absorbed increases as a result of its solution in the surface layers of platinum. Thus the activation energy of the diffusion of oxygen in platinum is apparently greater than the activation energy of desorption. Thus in Ref. 36, the value given for the activation energy of the diffusion of oxygen in platinum is $E_{diff} = 330 \pm 100$ kJ mole$^{-1}$. The formation and thermal stability of surface oxides of platinum may be influenced by impurities (Si, Ca).[37] Thus a calcium concentration corresponding to

1–2% of a monolayer at 300 K decreases when surface oxides are formed (curve *3*).

If a high concentration of oxygen is produced on a platinum surface, particularly on an "open" (321) face, the TD spectra, in addition to the usual broad $O_{ads}(I)$ peak (second-order desorption), show a new narrow peak with $T_{max} = 700$ K, whose position remains unchanged with variation of the degree of covering, that is first-order desorption takes place.[38] The appearance of this peak may be related to the decomposition of surface (2D) oxides of platinum.

*e) Adsorption on palladium*

When $O_2$ is chemisorbed on Pd(111), [39] the (2 × 2)O structure is formed at 300 K, but disappears on heating in a vacuum to 600 K. Heating at $T \geqslant 600$ K in a stream of $O_2$ leads to saturation of the surface region with oxygen and to the reappearance of the (2 × 2)O structure, attributed[39] to the production of the surface oxide PdO. On thermal desorption, two oxygen peaks were observed: the first is due to the recombination of $O_{ads}$ on the surface, and the second to the decomposition of the surface oxide.

In a PES study using synchrotron radiation,[40] the position of the O2*s* line indicated three states of oxygen, analogous to those found for platinum:[33] 1) $O_{ads}$ on "smooth" regions of the Pd(111) surface; this is realised in "pure" form at 150 K; 2) oxygen inserted into the surface layer of the metal, apparently at points of structural breakdown (defects, etc.), this $O_{ads}$ (type II, together with $O_{ads}$ of type I) is observed on Pd(111) at 300 K; and 3) surface palladium oxides, formed at 600–700 K.

## 2. Properties of Adsorption Layers of Types I and II

The above data make it possible to put forward a general adsorption scheme. When oxygen reacts with metals, a succession of surface compounds is formed:[14]

$$M + O_2(gas) \rightarrow M\text{-}O_{2\,ads} \rightarrow M\text{-}O_{ads}(I) \rightarrow M\text{-}O_{ads}(II) \rightarrow MO(oxide)$$
$$\qquad\qquad\qquad

non-reconstructive state $O_{ads}(I)$ possibly increases in the position of maximum coordination.

Adsorption of type I is thermodynamically more favourable in the series Ag–Ir. For Ru, Ni, Co, and other metals, the principal state is $O_{ads}(II)$, but at low degrees of covering on the most closely packed faces, the existence of reactive oxygen in the intermediate state $O_{ads}(I)$ is possible, and the oxygen atoms may not be in the position of maximum coordination.

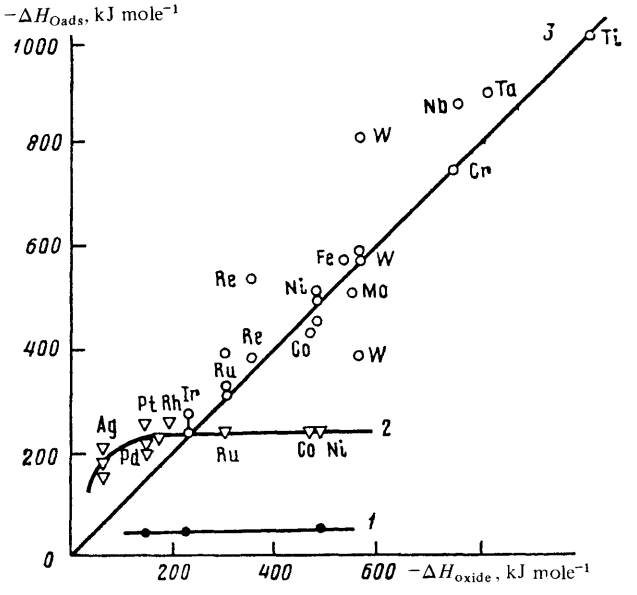



Figure 3. Plots of the heats of adsorption in the molecular (*1*), non-reconstructive (*2*), and reconstructive (*3*) forms against the heats of formation of the oxides of the corresponding metals.

The possibility of the transformation $O_{ads}(I) \rightarrow O_{ads}(II)$ depends on the energy of both the bonds being broken and the bonds being formed, and, in the general case, on the difference $\Delta H[O_{ads}(II)] - \Delta H[O_{ads}(I)]$. With decrease in the coordination number of the metal atoms in the series of structures: bulk (3D)–plane (2D)–step (1D), the heats of formation of the corresponding oxides apparently increase in the order:

$$|\Delta H[(1D)\text{oxide}]| > |\Delta H[(2D)\text{oxide}]| > |\Delta H[(3D)\text{oxide}]|$$

The insertion of an oxygen atom into a metal layer, that is the transformation $O_{ads}(I) \rightarrow O_{ads}(II)$, is accompanied by an increase in the effective charge on the atom, and its state changes from the radical-like state $O^{\delta-}_{ads}$ [19,55] to the state of oxygen in the surface oxide $O^{2-}_{ads}$. [19,40]

## III. THE OXIDATION OF CARBON MONOXIDE ON METALS

The investigation of the relationship between the kinetic and thermodynamic parameters of adsorption and heterogeneous-catalytic reactions is an important problem in the theory of heterogeneous catalysis.[56–58] The existence of a correlation between the heat of adsorption of oxygen and the catalytic activity of oxides in total oxidation reactions has been established.

The plot of the rate of the oxidation of CO against the energy of the bond formed by oxygen (Fig.4) is a curve with a maximum corresponding to the platinum group metals,[50] in agreement with the change in the rate of adsorption and the efficiency of the reaction in the same metal series.[59]

On metals for which the energy of the $M-O_{ads}$ bond is low (Ag, Au), the limiting stage is apparently the adsorption of oxygen. Thus a recent ESCA study[60] of the adsorption of oxygen on silver films (at an oxygen pressure up to 10 Pa) showed that the adsorption on the silver surface takes place with a low accommodation coefficient $s \cong 10^{-3}$ in a state characterised by a high reactivity towards CO (the efficiency of the reaction is close to 1). This agrees with published data.[61,62]

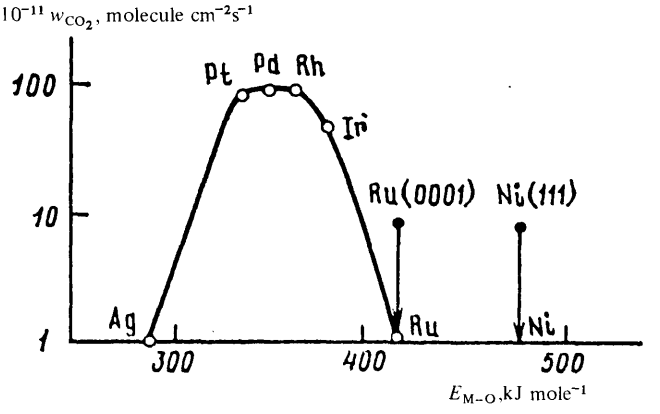



Figure 4. Plot of the rate of oxidation of carbon monoxide (520 K, $p(O_2) = p(CO) = 1 \times 10^{-5}$ Pa) against the energy of the bond formed by oxygen with metals; black points—catalytic activity of Ru(0001) and Ni(111) under non-stationary conditions.

For metals lying on the right-hand branch of the curve in Fig.4, the limiting stage is the reaction of CO with $O_{ads}$. Thus the adhesion coefficient of oxygen on Ru(0001) is 0.4, whereas the reaction rate at 520 K and $p(O_2) = p(CO) = 1 \times 10^{-5}$ Pa in the reaction mixture is only $2 \times 10^{11}$ molecule cm$^{-2}$ s$^{-1}$. [17] In Ref.63, the reaction rate on Ru(0001) under stationary conditions could not be measured at all ($w \leq 10^{11}$ molecule cm$^{-2}$ s$^{-1}$). Under stationary reaction conditions at pressures of oxygen and carbon monoxide of $1.3 \times 10^{-5}$ Pa on Ni(110), a layer of nickel oxide is formed.[64] Since it is highly endothermic ($\Delta H_p = 85$ kJ mole$^{-1}$), the reaction of $CO_{ads}$ with $O_{ads}$ on nickel takes place at a measurable rate only at temperatures above 600 K. The right-hand branch of the curve in Fig.4 agrees approximately with published data[65] which show that the rate of the oxidation of hydrogen decreases by a factor of $10^2$ on going from platinum to nickel.

An interesting feature is that under certain conditions at low temperatures, Ru(0001) and Ni(111) show a high but unstable activity (Fig.4).

### 1. The Influence of the Transformation $O_{ads}(I) \rightarrow O_{ads}(II)$ on the Activity of Ru, Ni, and Co

On the Ru(0001) face after a constant flux of the reaction mixture has been established ($p(O_2) = p(CO) = 1.3 \times 10^{-5}$ Pa)

with smooth increase in temperature (~1 K $s^{-1}$) from 300 K and above the formation of $CO_2$ is observed.[63,66] Fig.5 shows that the reaction rate is a maximum at 470 K. The catalytic activity is not constant, however, since keeping the specimen at any temperature leads to a decrease in the reaction rate. As already noted, oxygen is adsorbed on Ru(0001) at 300 K in a reactive form (type I), which on heating is converted into a surface oxide (type II), leading to the suppression of the catalytic activity. The kinetics of oxidation of CO on Ru(0001) have been described using the observed rate constants for the stage of the adsorption of $O_2$ and CO, the reaction $O_{ads}$ + $CO_{ads}$, and the stage corresponding to the irreversible transformation $O_{ads}(I) \rightarrow O_{ads}(II)$.[66]

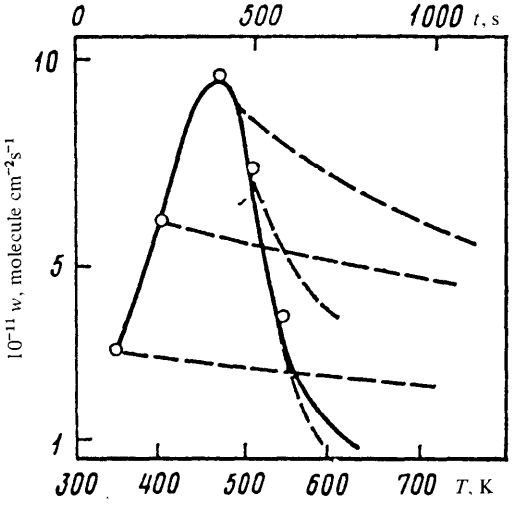



**Figure 5.** Temperature dependence of the rate $w$ of formation of $CO_2$ on the Ru(0001) face for a specimen heated at a rate of 1 K $s^{-1}$. The points correspond to the specimen heated at the given temperature, and the broken lines correspond to the change in $w$ with time.

When Ni(111) is cooled slowly from 800 K or kept under isothermal conditions at 450–500 K in the reaction mixture (5% $O_2$) a "burst" of catalytic activity is observed during the phase transformation Ni(111) → NiO.[14,67] In the case of Ni(100) under the same conditions, this "burst" is not observed. It is possible that on Ni(111) the reaction involves $O_{ads}(I)$, and that the surface region before the "burst" is gradually saturated with dissolved oxygen, preventing the diffusion of $O_{ads}(I)$ into the volume, so that the activity increases. The subsequent decrease in catalytic activity is due to the formation of a surface oxide. Essentially analogous data have been obtained[68] for the Co(0001) face.

Thus for metals such as Ru, Ni, Co, etc., the initial high catalytic activity associated with the production of $O_{ads}(I)$ gradually decreases as a result of the conversion of $O_{ads}(I)$ into the surface-oxide state (type II), in which the oxygen is unreactive under the given conditions.

## 2. The Oxidation of CO on Metals of the Platinum Sub-group

The oxidation of CO on metals of the platinum sub-group, which have a high catalytic activity under stationary conditions, can be considered.

### *a) Titration of the adsorbed oxygen with carbon monoxide*

The (111) and (110) faces of a single crystal of Ir show a high specificity in the titration, that is the differences between the faces are extremely marked. Thus on Ir(111) the initial rate of the titration ($w^0$) is low at 300–400 K [69] and with increase in temperature it increases in proportion to the decrease in the intensity of the reflections of the (2 × 2)O structure, that is the degree of disorder in the (2 × 2)O layer. On an Ir(110)–(1 × 3) surface micro-faceted by (111) faces, the initial rate remains high ($w^0 \cong 10^{12}$ molecule $cm^{-2}$ $s^{-1}$) at 300–400 K, that is at temperatures below the temperature at which disorder is produced in the (2 × 2)O layer. Thus on Ir(111) the reaction requires thermal disordering of the layer, whereas on Ir(110)–(1 × 3) the structure of the surface itself plays the role of the factor producing structural disorder. The high value of $w^0$ on Ir(110), from the viewpoint of formal kinetics, can be described in terms of the Eley–Rideal mechanism with $E$ = 2–4 kJ $mole^{-1}$, although in fact the reaction takes place in the adsorption layer,[70–72] possibly with the participation of oxygen adsorbed on the edges of the micro-facets.

If the stream of CO is interrupted during the titration of $O_{ads}$ on iridium and on a stepped platinum surface Pt(s), heating the specimen gives $CO_2$ as a result of the reaction $O_{ads}$ + $CO_{ads}$.

For Ir(111), one "low-temperature" α-$CO_2$ peak is observed. Conversion of the temperature dependence of the rate of formation of $CO_2$ at this peak to a straight line in the coordinates lg $w/[O][CO] = f(1/T)$ gives the values of the constants $E_a$ = 44 kJ $mole^{-1}$, $k_a^0 = 10^{-10}$–$10^{-11}$ $cm^2$ molecule$^{-1}$ $s^{-1}$. For Ir(110)–(1 × 3), two peaks are observed: an α-$CO_2$ peak with constants close to those found for Ir(111), and a "high-temperature" β-$CO_2$ peak, which can probably be related to oxygen introduced into the metal in the "valleys" of the micro-facets.

For a stepped platinum surface,[73] the following values were obtained: for α-$CO_2$, $E_a$ = 40 kJ $mole^{-1}$, $k_a^0 = 10^{-3}$ $cm^2$ molecule$^{-1}$ $s^{-1}$; for β-$CO_2$, $E_a$ = 80 kJ $mole^{-1}$, $k_a^0 = 10^{-6}$ $cm^2$ molecule$^{-1}$ $s^{-1}$. The β-$CO_2$ peak can be assigned to the reaction of $CO_{ads}$ with oxygen reconstructively adsorbed on the steps of the surface. Thus it has been shown[33] that the oxygen in the 2(1D)O structure on Pt(s) is less reactive than the $O_{ads}(I)$ on the terraces. Field-emission microscopy[74] previously showed that the reaction of CO with $O_{ads}$ on platinum points, the surface of which consists chiefly of "open" faces and faces with a high density of steps, takes place at temperatures of 400–500 K, in agreement with the temperature range of β-$CO_2$ formation. In the region of the Pt(201) faces, the boundary of the reaction was gradually displaced.

### *b) The oxidation of CO under stationary conditions*

The kinetics of the oxidation of CO on Ir(110) and platinum can be described by a two-path scheme (Langmuir–Hinshelwood and Eley–Rideal mechanisms) using the observed rate constants of the separate stages.[14,75] Agreement between the calculated (curve *1* in Fig.6) and experimental temperature dependence of the reaction rate could be achieved only if it was assumed that the activation energy of the desorption of CO corresponds to the most firmly bound form β-$CO_{ads}$, indicating the importance of the presence of steps (defects) for the reaction on metals of the platinum group. It can be seen from Fig.6 (curve *2*) that the increase in the rate over the range 480–525 K is effectively described by the Langmuir–Hinshelwood mechanism alone; the introduction of the Eley–Rideal mechanism is required to describe the reaction at

higher temperatures. It follows from the SED data at $T \geq 500$ K, however, that the Ir(110)–(1 × 3) surface is transformed into a surface oxide Ir(110)–(1 × 1)O, leading to a change in the constants for all the stages and to the appearance of hysteresis on going from the "forward" to the "reverse" change in temperature.

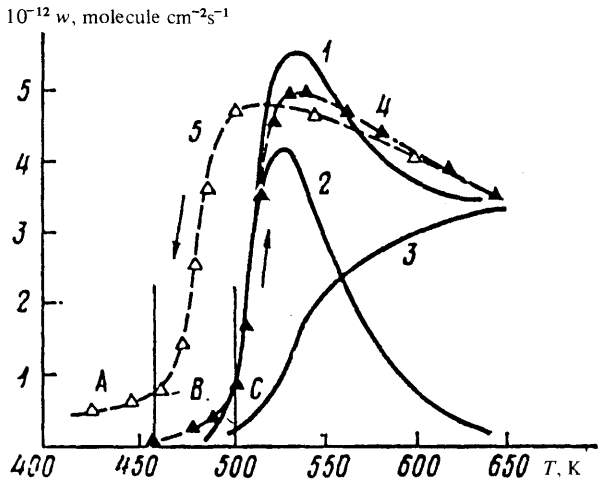



**Figure 6.** Temperature dependence of the rate of oxidation of CO on Ir(110) under stationary conditions (treatment for 5 min at each point; $p(O_2) = 1.6 \times 10^{-5}$ Pa, $p(CO) = 6.7 \times 10^{-6}$ Pa); *1–3*) calculated curves: *1*) overall rate, *2*) rate for the Langmuir–Hinshelwood mechanism, *3*) rate for the Eley–Rideal mechanism; *4, 5*) experimental curves: *4*) on heating, *5*) on cooling. The ranges of existence of the structures (1 × 3), 2(1D)O, and (1 × 1)O are denoted by the letters *A*, *B*, and *C* respectively.

On platinum in an excess of oxygen, for example at $p(O_2)/p(CO) = 5$, ($p(CO) = 2.6 \times 10^{-6}$ Pa), under stationary conditions (time of treatment at each point 5 min), hysteresis is also observed for the "forward" and "reverse" change in temperature (Fig. 7*a*).[73] This hysteresis is not truly kinetic in character, due to non-linearity of the stages involving the adsorption of $O_2$ and the reaction in the adsorption layer, as assumed in Ref. 76, since decrease in temperature from different initial points of the curve for the "forward" change in temperature gives different curves for the "reverse" change.[73] The hysteresis is evidently related to a change in the state of the oxygen on platinum.

Preliminary solution of oxygen at $T \approx 800$ K (see Fig. 2*c*) has no influence on the course of the $w = f(T)$ curves. Thus the hystersis is related to surface processes. Figs. 7*b* and 7*c* give the titration curves for oxygen adsorbed on platinum under stationary reaction conditions, obtained after the flow of oxygen had been stopped. Stopping the flow of $O_2$ at 430–460 K (Fig. 7*b*) leads to a sharp decrease in the rate, but at $T \geq 500$ K the curves are flat. The concentrations of $O_{ads}$ obtained from the titration curves at 445 K are less than $10^{12}$ atom cm$^{-2}$, and at 600 K the value obtained was ~$5 \times 10^{13}$ atom cm$^{-2}$. The order of magnitude of the last value ($\theta = 0.05$) agrees with the density of steps. Under stationary reaction conditions at 500–600 K and during the titration (flat regions), the SED patterns show "bands" of the 2(1D)O structure. On cooling (see Fig. 7*c*), the proportion of flat regions on the titration curves, and the stationary concentration of inserted $O_{ads}$(II), are much greater than those for the "forward" change (Fig. 7*b*).

Thus at 300–400 K, the $CO_{ads}$ molecules apparently block the Pt(s); at 400–460 K, the desorption of β-$CO_{ads}$ liberates the steps on which $O_2$ dissociates, and the $O_{ads}$(I) form reacts immediately with $CO_{ads}$. At $T \geq 480$ K, as a result of the transformation $O_{ads}(I) \rightarrow O_{ads}(II)$, the reaction no longer takes place on the steps (defects), but on the one-dimensional platinum oxide (1D)O.

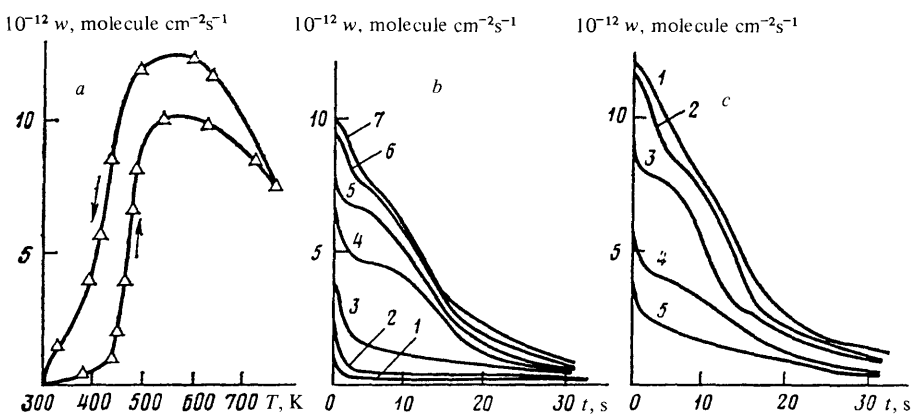



**Figure 7.** *a*) Temperature dependence of the rate of the oxidation of CO on platinum foil under stationary conditions ($p(O_2) = 1.3 \times 10^{-5}$ Pa, $p(CO) = 2.6 \times 10^{-6}$ Pa; *b*) titration curves for oxygen adsorbed under stationary reaction conditions (*a*), obtained after switching off the stream of $O_2$ during the "forward" change in temperature (heating). Temperatures of the titration, K: *1*) 430, *2*) 445, *3*) 460, *4*) 480, *5*) 495, *6*) 540, *7*) 600. *c*) The same for the "reverse" change in the temperature of the reaction (*a*). Temperatures of the titration, K: *1*) 535, *2*) 485, *3*) 450, *4*) 400, *5*) 340.

## 2. General Scheme for the Oxidation of CO on Metals

The equation for the reaction rate can be written in the following general form:[5]

$$w = k\mathrm{f}(c_i\theta_i)\,\varphi(c_i)\ .$$

The first term is determined by the stoichiometry of the active complex, and the second by the influence of the reaction medium on the properties of the catalyst. For the oxidation of CO, the set of stages determining the kinetics of the reaction on a non-changing surface (that is without allowance for the influence of the reaction medium) can be written as the four-stage scheme:[75-77]

$$O_2 + 2Z \xrightarrow{k_1} 2ZO \qquad (1)$$

$$CO + Z \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} ZCO \qquad (2)$$

$$ZO + ZCO \xrightarrow{k_3} CO_2 + 2Z \qquad (3)$$

$$ZO + CO \xrightarrow{k_4} CO_2 + Z \qquad (4)$$

Here, Z represents the adsorption centres on the metal surface. Stage (3) corresponds to the Langmuir–Hinshelwood mechanism, and stage (4) to the Eley–Rideal machanism. As already noted, the collision stage (4) in this model is introduced to describe the kinetics at high temperatures (see Fig.6), but oxidation of the metal already takes place under these conditions. In this scheme, ZO represents the radical-like[19,55] non-reconstructively adsorbed $O_{ads}(I)$.

The influence of the reaction medium ($\phi(c_i)$) is related to the oxidation of the metal in the stages:

$$ZO \xrightarrow{k_5} Z_{ox}O\,, \qquad (5)$$

$$Z_{ox}O + ZCO \xrightarrow{k_6} CO_2 + Z'_{ox} + Z\,. \qquad (6)$$

Here, $Z_{ox}$ represents the centre of the surface oxide associated with $O_{ads}(II)$, and $Z'_{ox}$ the same centre in the intermediate state after the removal of $O_{ads}(II)$ by reaction with $CO_{ads}$ (stage (6)).

For metals such as Ru and Ni, the rate constants of stage (6) are low compared with $k_3$ and $k_4$, so that the transformation $O_{ads}(I) \rightarrow O_{ads}(II)$ (stage (5)) leads to the suppression of the catalytic activity.

For the platinum metals, the constants $k_6$ and $k_3$ do not differ so greatly.[73] Thus for Pt(s) the ratio of the rate constants for the reaction of $CO_{ads}$ with $O_{ads}(I)$ and $O_{ads}(II)$ at 500 K is $k_3/k_6 = 10-10^2$, so that reaction is possible under stationary conditions. Oxidation of the metal naturally also changes the values of the constants of stages (1) and (2); the rates of the adsorption of $O_2$ and CO decrease slightly, and, which is more important, the heat of adsorption of $CO_{ads}$ decreases; as a result, $CO_{ads}$ blocks the surface at lower temperatures, and this is responsible for the hysteresis. Recently, a similar scheme (stages (1)–(6)) was used to obtain a quantitative description of the self-oscillations in the rate of the oxidation of carbon monoxide on platinum and iridium.[78,79]

Next, the displaced metal atoms ($Z'_{ox}$) formed in stage (6) apparently either return to their equilibrium position on the step (Z) or "roll out" on to a terrace, forming so-called adsorbed metal atoms $Z_{ads}$

$$Z'_{ox} \xrightarrow{k_7} Z\,, \qquad (7)$$

$$Z'_{ox} \xrightarrow{k_8} Z_{ads}\ . \qquad (8)$$

The appearance of thermodynamically unstable forms ($Z_{ads}$) under stationary conditions as a result of the heat of the reaction may have a significant influence on the catalytic properties of the metal.[80] The adsorbed atoms (or clusters) $Z_{ads}$ can act as new "active centres" for the adsorption of $O_2$, bringing about a branched-chain process.[81] The heat of the reaction $O_{ads} + CO_{ads}$ on platinum is $\Delta H_p = -(30-50)$ kJ mole$^{-1}$, that is it is even lower than the energy of a single Pt–Pt bond (85 kJ mole$^{-1}$).[82] In view of the high rate of the dissipation of energy in the metal lattice, it is difficult to imagine that the reaction between $CO_{ads}$ and $O_{ads}(I)$ can lead to the "ejection" of metal atoms, that is to the formation of $Z_{ads}$. In the case of reconstructive chemisorption, however, even at the stage of the insertion of oxygen into the layer of metal (stage (5)), displacement of platinum atoms (or at least a decrease in the strength of the Pt–Pt bond) takes place, so that the reaction stage (stage (6)) only facilitates the removal of platinum atoms. Thus the formation of $O_{ads}(II)$ is a necessary condition for the processes involved in the rearrangement of the surface.

Scanning microscopy has shown[83,84] that the oxidation of CO produces a marked change in the micro-relief of the surface of a platinum filament, although the adsorption of $O_2$ or CO alone has no significant influence on the surface. It is easy to imagine that if the rate of generation of $Z_{ads}$ is high, and the rate of their diffusion over the terraces is low, then "loosening" of the surface will take place. If however the rate of diffusion is high, the $Z_{ads}$ atoms will be able to migrate to the positions with minimum free energy, and completion of the most closely packed faces (facetting) will take place.

## 4. The Specific Features of the Faces in Catalysis and the Constancy of the Specific Catalytic Activity

The specific features of the faces and "active" centres in catalysis and the constancy of the specific catalytic activity have been examined.[5,14,59]

The rate of the reaction of $H_2$ with oxygen adsorbed in the Ni(111)–(2 × 2)O structure is 10–20 times the rate of the reaction with $O_{ads}$ in the Ni(100)–c(2 × 2)O structure. The rearrangement of Ni(111) to the Ni(100)–c(2 × 2)O//Ni(111) structure, however, leads to approximately equal reactivities of oxygen on the two faces.[14,59]

The reaction of CO with $O_{ads}$ on Ir(110) at 330 K is ten times that on Ir(111). In a reaction stream with relatively rapid heating of the specimens (~4 K s$^{-1}$), the Ir(110) to (1 × 3) face is 2.5 times more active than the Ir(111) face. Under stationary reaction conditions, surface oxides are formed, the Ir(110)–(1 × 3) surface at $T \geq 450$ K is rearranged to the (1 × 1)O structure, and the catalytic activities of the two faces become equal.[14,28,59]

Thus if under the reaction conditions (relative excess of CO, comparatively low temperatures) the oxygen on the surface is adsorbed as $O_{ads}(I)$, then the structure of the surface is important for the reaction, the steps act as "active" centres, and the actual reaction takes place via stages (1)–(4). At "high" temperatures with an "excess" of oxygen in the reaction mixture, $O_{ads}(II)$ is formed on the surface, stages (5)–(8) also take place, and rearrangement of the surface leads to the practical disappearance of the specific characteristics of the faces, that is the rule of approximate constancy of the specific catalytic activity is observed.

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Thus examination of the properties of the two most important types of adsorbed oxygen, namely the non-reconstructive (I) and the reconstructive (surface-oxide) (II) types, has made it possible to explain a number of phenomena of oxidative catalysis on metals in a single scheme.

This approach may be more general, since in addition to adsorption layers of type I (sulphur, nitrogen, carbon), surface sulphides, nitrides, and carbides are also known for metals.

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# The Application of Mössbauer Spectroscopy to the Study of Tin-containing Catalysts

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The principal problems arising in the study of tin-containing homogeneous and heterogeneous catalysts by Mössbauer spectroscopy are reviewed. The information provided by the parameters of the method, among which special attention has been devoted to the probability of the resonance absorption of $\gamma$-quanta by the specimen and its temperature variation, is analysed. The principal results obtained in the study of the structure and properties of various tin-containing catalysts are surveyed.
The bibliography includes 91 references.

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## I. INTRODUCTION

Specific types of tin(II)-containing compounds have now gained a firmly established place among homogeneous and heterogeneous catalysts of various processes in reductive media. $SnCl_3$-containing transition metal complexes are most widely used as homogeneous catalysts. Platinum metal complexes, both those in which the ligands are tin halide species alone and complexes containing $PR_3$, $P(OR)_3$ and CO molecules in addition to Cl and $SnCl_3$, exhibit catalytic properties in the hydrogenation reactions of various monoolefins and polyolefins as well as unsaturated organic acids, in their isomerisation, in olefin carboxylation processes, etc. Most detailed information on this question has been published by Matvienko.[1] On the other hand, industrial catalytic processes are mainly carried out on deposited Pt–Sn intermetallic compounds, which are used in reforming[2] and dehydrogenation[3] processes.

The unique possibilities of the Mössbauer method for securing information about the structure and properties of tin-containing compounds have been known for a long time.[4] However, its application to the study of such catalysts has been inadequately dealt with in review articles. One of the first reviews in which questions concerning the application of Mössbauer spectroscopy to catalysis were discussed dealt largely with iron compounds[5] and concentrated mainly on two possible aspects of the application of the Mössbauer effect: (1) the derivation of information about the electronic states of the atoms in catalysts and about the relation with their activity and selectivity; (2) the detection of intermediate complexes in catalysis. The only study considered by Gol'danskii and Suzdalev[5] was that of Skalkina et al.[6], who found that the relation between the rate of the oxidative ammonolysis of propene and quadrupole splitting $\Delta$ (for a constant chemical shift $\delta$) has an extremum for $SnO_2$ and its solid solutions in $Sb_2O_4$, $MoO_3$, and $Fe_2O_3$.

The most complete review, in the sense of coverage of problems involving catalysis, is that of Dumesic and Topsoe,[7] who discuss in detail the information contained in the parameters of the Mössbauer spectra, the characteristic features of the application of the method to the study of the structure of the catalyst surface, the adsorption of various molecules on such a surface, and the reactivity of molecules containing different Mössbauer atoms. Their review covers an even greater number of examples of the study of tin-containing catalysts, but these are mainly tin(IV) compounds. In a later review[8] dealing with the application of Mössbauer spectroscopy to catalysis, no information whatever is included about tin-containing catalysts. Finally, the compilations of communications on Mössbauer spectroscopy, regularly published in the journal Analytical Chemistry (R) (see, for example, Stevens et al.[9]) are concerned with all the aspects of the application of the method and do not analyse the characteristics of its application to the study of particular types of systems, including catalysts.

This position can be partly accounted for by the fact that the number of studies on tin-containing catalysts by the Mössbauer method has indeed been small. For example, the first investigation of the industrial tin-containing catalysts deposited on $\gamma$-$Al_2O_3$ appeared in 1975.[10] The authors[10] showed that the surface of the carrier contains a whole set of tin (IV), tin(II), and zerovalent tin compounds, although the main problem is their detailed identification. Studies of this kind have been partly discussed in a recently published review,[11] but the methodological aspect of the problem of the determination of the number of individual components of the catalyst, their composition, and their state on the basis of the complex overall Mössbauer spectrum remained inadequately dealt with.

The experience gained in the application of physical methods to catalysis, accumulated at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences, has shown that a fairly profound understanding of the reaction mechanism and of the action of the active centre has been achieved in those cases where it was possible to obtain reliable information about its composition, structure, or the type of compound or phase constituting this centre. One must note that none of the reviews published hitherto has considered the outcome of the application of the Mössbauer effect to the study of tin-containing homogeneous catalysts. Here too it is necessary to obtain in the first place information about their composition and structure. In view of the foregoing, in the present review we shall consider primarily the structural aspect of the application of the Mössbauer method to the study of tin-containing homogeneous and heterogeneous catalysts.

## II. METHODOLOGICAL PROBLEMS IN THE STUDY OF CATALYSTS BY THE MÖSSBAUER METHOD

In this Section, no attempt is made to describe all the methodological problems of the application of the Mössbauer effect in chemistry; like the theory of the method, they have been described in detail elsewhere.[12–16] Here we shall deal only with those of their aspects which are most important for the investigation of catalysts.

### 1. Homogeneous Systems

As mentioned above, the homogeneous catalysts usually consist of $SnCl_3$-containing platinum metal complexes as well as clusters of the same metals incorporating $SnCl_3$, $SnCl_2$, and SnCl groups and Sn atoms.[1,17,18]

It has been shown[17–20] that the line form in the Mössbauer spectra of complex compounds frequently differs from the ideally symmetrical doublet; this can be caused by the non-equivalence of the positions (and hence the electronic structures) of the $SnCl_3$ ligands in the coordination sphere of the platinum metal or, which happens more frequently, by the presence in its coordination sphere of tin-containing ligands of different composition. The latter is typical for clusters.[17,18,21] In this case the determination of the parameters of the Mössbauer signal of each kind of tin-containing groups makes it necessary to resolve the overall spectrum into individual doublets with a Lorentzian line form. Fig. 1 (Yurchenko[18]) presents the Mössbauer spectrum of the $[Pd_3Sn_8Cl_{20}]^{4-}$ cluster obtained in the form of the tetraphenylphosphonium salt; the spectrum was interpreted on a BESM-6 computer. The line form of each quadrupole doublet was described by the expression

$$W_a(E) = \frac{1}{2\pi}\left[\frac{\Gamma_{nat}/2}{(E-E_0-\Delta)^2+(\Gamma_{nat}/2)^2}+\frac{\Gamma_{nat}/2}{(E-E_0+\Delta)^2+(\Gamma_{nat}/2)^2}\right], \quad (1)$$

where $E$ is the energy of the emission of $\gamma$-quanta, $E_0$ the energy of the resonance transition, and $\Gamma_{nat}$ the natural line width.

Later it was found that it was more rational to carry out an analogous resolution procedure with the aid of an SK-2 curve synthesiser,[18] which makes it possible to isolate simultaneously up to seven components of the spectrum. The area under the envelope of each doublet is related to the number of absorbing atoms $n$ by the familiar expression[14,15,17]

$$S_a = \frac{\pi}{2}\Gamma_{nat}\sigma_0 \varkappa f n f', \quad (2)$$

in which $\varkappa f$ can be determined by the black absorber method, which has been described for tin.[22] Yurchenko[18] adopted $f'_{77} = 0.22$ for the $SnCl_3$ ligand, 0.3 for SnCl, and 0.4 for Sn in the $Pd_3Sn$ alloy.[23] Taking into account these values of $f'$ for Sn in $[Pd_3Sn_8Cl_{20}]^{4-}$, it is found that the ratio of the areas of the two doublets in Fig. 1 corresponds to the ratio of the numbers of tin atoms in the ligands of the cluster, which is 3:1;[18,21] this constitutes one of the arguments in support of the representation of the composition of the cluster by $[Pd_3(SnCl_3)_6(SnCl)_2]^{4-}$.[21]

The study of the state of catalysts under the conditions of the catalytic process (*in situ*) is particularly valuable. For homogeneous systems, this requires the measurement of the Mössbauer effect for solutions, which, by virtue of the nature of the effect itself, becomes possible only when the latter are frozen. In those cases where the concentration of the catalytically active forms of the complex or intermediate states is high, freezing of the solutions has a conserving effect on these forms and makes it possible to identify them from the Mössbauer spectra. However, studies available hitherto on the Mössbauer spectroscopy of frozen solutions have been associated mainly with the analysis of complex formation processes.[24–27] In their methodological aspect, such studies require the availability of cells of appropriate design, which would not break on cooling the solution to the temperature of the liquid nitrogen and would retain their hermetic seal.

The use of Mössbauer parameters such as $\delta$ and $\Delta$ for the identification of the types of complexes predominating in solution required the accumulation of information about the characteristics of the Mössbauer effect for compounds of tin in various oxidation states and with different structure of its immediate environment. For tin(II) complexes, such a study has been carried out[18] and the relation between the observed changes in the Mössbauer parameters and the characteristics of the structure of the complex as a whole and of the tin(II)-containing ligands in it has been elucidated by simultaneous investigation of the crystals of the complexes by the X-ray diffraction and Mössbauer spectroscopic methods. Fig. 2 presents examples of the Mössbauer spectra of various tin compounds; evidently, the values of $\delta$, $\Delta$, the width of the components $\Gamma$, and the form of the spectra are sensitive not only to changes in the oxidation state of tin but also to the characteristics of the structure of the tin-containing compounds.[17] Thus the formation of a coordinate bond by the $SnCl_3$ group alters $\delta$ from 3.64–3.00 mm $s^{-1}$ and $\Delta$ from 0.90–1.73 mm $s^{-1}$ for the $SnCl_3^-$ ion[28] to 1.50–1.95 mm $s^{-1}$

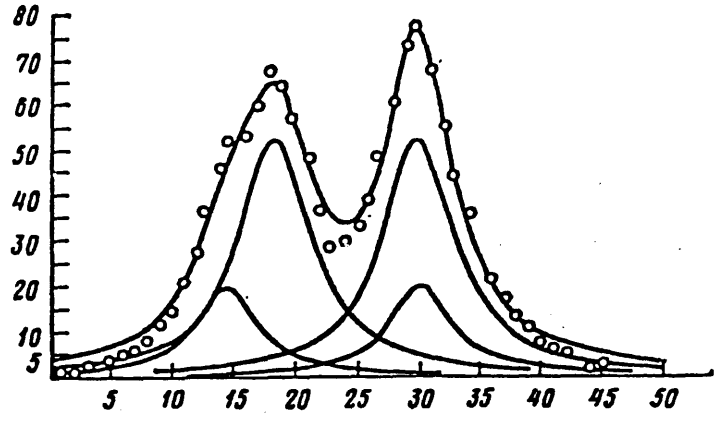



**Figure 1.** The Mössbauer spectrum of the $(Ph_4P)_4[Pd_3Sn_8Cl]_{20}$ cluster (in terms of the arbitrary units of the graph plotter.

and 1.60–2.10 mm $s^{-1}$ respectively.[29–35] If all the $SnCl_3$ ligands in the coordination sphere of the complex have equivalent positions and geometries, as, for example, in $[PdCl_3(SnCl_3)]^{2-}$ (Fig. 2, curve 3), then under these conditions a symmetrical doublet is observed with lines of equal and minimum width. If the ligands in the coordination sphere of the complex occupy non-equivalent positions, for example, the axial and equatorial $SnCl_3$ groups in $[Pt(SnCl_3)_5]^{3-}$, and therefore have different values of $\delta$ and $\Delta$, then the overall spectrum can be asymmetric and can have broader lines (Fig. 2, curve 4). Finally, the presence of tin(II)-containing ligands in the complex which are non-equivalent as regards composition and structure imparts a strongly asymmetric contour to the overall spectrum resulting from the doublets due to each ligand (Fig. 2, curve 5).

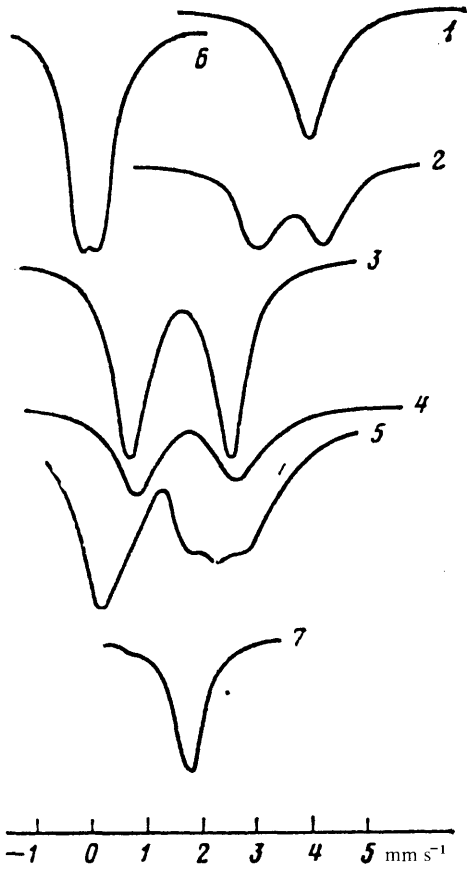



**Figure 2.** Mössbauer spectra: 1) $SnCl_2$(anh.); 2) $SnCl_2 \cdot 2H_2O$; 3) $(Ph_4P)_2[PdCl_3(SnCl_3)]$; 4) $(Et_4N)_3[Pt(SnCl_3)_5]$; 5) $Cs_4[Rh(Sn_4F_{15})(SnF_2(H_2O)_2]_2 \cdot 2H_2O$; 6) $SnO_2$; 7) PtSn.

The non-equivalence of the $SnCl_3$ ligands as regards their positions in the coordination sphere of the complex affects the form of the spectrum to a greater extent than the differences between the geometries of each of them. This has been demonstrated by an investigation[36] of the crystal structure and spectra of $[Me_4N]_4[OsCl(SnCl_3)_5]$. All ten crystallographically independent $SnCl_3$ ligands in the unit cell of the crystal of this compound have appreciably different SnCl bond lengths and Cl–Sn–Cl angles. Nevertheless, the Mössbauer spectrum of the powdered complex consists of a symmetrical doublet;[32] the above differences in the geometry of the $SnCl_3$ groups induce only a broadening of the line widths to 0.85 mm $s^{-1}$.

Thus the results of a number of studies[30–36] helped to discover how much structural information is contained in the Mössbauer characteristics of tin(II) compounds, such as the form and width of the components of the recorded spectrum and the values of $\delta$ and $\Delta$ for its individual components. Dynamic parameters, particularly $f'$, have not been used to characterise the structural features of tin-containing catalysts.

The quantity $f'$ is defined by the expression

$$f' = \exp\left(-\frac{\langle x^2\rangle}{\lambda^2}\right), \qquad (3)$$

where $\langle x^2\rangle$ is the mean square shift of the emitting nucleus at the crystal lattice site in the direction of the stream of $\gamma$-quanta. $\lambda = \lambda/2\pi$, and $\lambda = 0.52$ Å for $^{119}Sn$. One might expect that the characteristics of the structure of tin-containing compounds will be reflected in the value of $\langle x^2\rangle_{Sn}$ for the latter and hence in the value of $f'$.

The parameter $f'$ is, in principle, related to the macroscopic properties of the entire crystal containing the Mössbauer atom.[13,14] The value of $f'$ in the range $1 \leq f' \leq 0$ depends on whether there exist in the given crystal possibilities for the consumption of part of the energy of the $\gamma$-quanta, which is equal to the recoil energy of the Mössbauer nucleus. Such energy dissipation channels are provided by the excitation of the phonon spectrum and of the individual vibrations of the crystal in the optical branches.[37,38] In simplest cases of one- or two-atom lattices, the Debye model of the solid is used for the description of $f'$,[39] according to which we have in the temperature range above 77 K

$$f' = \exp\left(-\frac{6E_R T}{k\Theta^2}\right), \qquad (4)$$

where $\Xi$ is the characteristic Debye temperature for the crystal, $E_R$ the recoil energy, and $k\Xi = \hbar\omega_{max}$.[12–14] It has been suggested that, when the Mössbauer nucleus in the solid forms part of the composition of the molecule or ion having characteristic vibration frequencies $\omega_i$, Einstein's model of the solid be employed, according to which

$$f' = \prod_i \exp\left(-\frac{E_R}{\hbar\omega_i}\coth\frac{\hbar\omega_i}{2kT}\right). \qquad (5)$$

It has also been suggested[40] that $f'$ for molecular crystals be expressed as the product $f'_{ia}f'_{ir}$, where $f'_{ia}$ characterises the component of the probability of the absorption of a $\gamma$-quantum which depends solely on the intramolecular vibrations of the Mössbauer atom, while $f'_{ir}$ characterises the part which depends on the vibrations in the solid of the entire molecule containing the given atom. Eqn. (3) is then valid for $f'_{ia}$ and $f'_{ir}$ separately, $\langle x^2\rangle_{ir}$ is a result of the shift of the Mössbauer atom as a consequence of intermolecular vibrations, and $\langle x^2\rangle_{ia}$ is the result of the shift due to intramolecular vibrations. A number of compounds, for example organotin(IV) compounds, have high frequencies (300–400 $cm^{-1}$ and above) and, in conformity with Eqn. (4) or (5), $f'_{ia} \to 1$. Debye's model of the solid state is usually employed to describe $f'_{ir}$ and the following relation is analysed:

$$\frac{d\ln f'}{dT} = \frac{3E_i^2 k}{M_{eff}c^2\hbar^2\omega_i^2}, \qquad (6)$$

where $M_{eff}$ is the mass of the entire molecule and $\omega_i$ its

vibration frequency (the lowest lattice vibration frequency is adopted as $\omega_i$). In combination with the determination of $\omega_i$ from Raman spectra, this approach has been used in a whole series of studies, for example, for the determination of the molecular weights of tin-containing compounds.[41-45]

It follows from Eqns.(4)–(6) that the higher the effective mass of the vibrating molecule and the lower the vibrational frequency of the Mössbauer atom, the closer is $f'$ to unity and the weaker the dependence of $f'$ on $T$.

However, the above approach proved to be unsuitable for a whole series of systems. For example, in biological objects containing the $^{57}$Fe label a marked dependence of $f'$ on $T$ (over a limited temperature range) and of the absolute value of $f'$ on the water content in the protein has been observed.[46,47]

It is also noteworthy that, in an early study[48] of the Mössbauer effect in amorphous tin halide compounds, it was observed that the absorption of $\gamma$-quanta without recoil does not require the presence of a crystal structure as such. It is only necessary that an effective mechanism hindering the consumption of the energy of the $\gamma$-quanta in the form of the recoil energy in different kinds of low-frequency rotational and vibrational movements of the groups containing the Mössbauer atom should operate.

In terms of the structural aspects of the use of Mössbauer spectroscopy in which we are interested, it was extremely important to elucidate to what extent the parameter $f'$ itself and its dependence on $T$ are determined by the internal structure of the tin-containing molecule and why this is so. In order to solve such a problem, it is essential to have information about the crystal structures of various tin(II) halide complexes of transition metals. Such data have been obtained in a number of studies.[19,36,49-53] They show that all tin-containing halide complexes without exception are constructed according to the principle of molecular crystals, i.e. the interaction energies of the atoms within the complex anion and within the cation (short interatomic contact) greatly exceed the energy of interaction between them (long interatomic contact). The structure of the (Sn–F)-containing anion is such that four Sn atoms are linked via bridging F atoms. In the chlorine complexes tin is present in the form of the $SnCl_3$ ligand, but the geometry of the latter within the anion and within the unit cell and also in different compounds can vary significantly.

A study[17,54] of $f'$ and of its dependence on $T$ for the number of (Sn–F)-, (Sn–Cl)-, and (Sn–Br)-containing complexes has shown that the maximum values of $f'$ and its weakest temperature dependence ($f'_{77} = 0.5$, $f'_{77}/f'_{153} = 1.6$),† close to that obtained for platinum–tin and nickel–tin alloys, are observed for the fluorides. For the $SnCl_3$-containing complexes, the values of $f'$ are lower and their dependence on $T$ is more marked ($f'_{77} = 0.2$, $f'_{77}/f'_{153} \cong 4-5$). For the $SnBr_3$-containing analogues with the same cations, the values of $f'_{77}$ are somewhat greater (0.3), but the dependence of $f'$ on $T$ is steeper ($f'_{77}/f'_{153} \cong 6$). In a series of compounds of the same $SnCl_3$-containing complex anion, the increase of density from 1.8–2.2 g cm$^{-3}$ to 3.3 g cm$^{-3}$ on replacement of the bulky organic cation by $Cs^+$ entails an increase of $f'_{77}$ to 0.4 and a weakening of its temperature dependence ($f'_{77}/f'_{153} = 3$); however, in this case too $f'$ is smaller and its dependence on $T$ is stronger than for the fluorides. For frozen fluoride solutions, the values of $f'$ are also higher than for the chlorides. This demonstrates that the measured $f'_{eff}$ for the crystalline complexes investigated depend both on the internal properties of their tin-containing anions and on the characteristics of the interionic interaction in the crystal as a whole, i.e. both on $f'_{ia}$ and on $f'_{ir}$.

The components of the effective mean-square vibration amplitude of the tin atom in the crystal lattices of such ($\langle x^2\rangle_{eff}$) have been analysed:[55]

$$\langle x^2\rangle_{eff} = \langle x^2\rangle_{ia} \coth\frac{\alpha_{ia}}{T} + \langle x^2\rangle_{i\gamma} \coth\frac{\alpha_{i\gamma}}{T}, \qquad (7)$$

where $\alpha_{i(j)} = \hbar\omega_{i(j)}/2k$, $\omega_i$ the frequency of the lowest-frequency vibration of the Mössbauer atom within the molecule, and $\omega_j$ the frequency of its vibration together with the molecule. This equation was first used to analyse the dynamics of the behaviour of the tin atom on the silica gel surface.[56]

The observed[55] $\langle x^2\rangle_{eff}$–$T$ relations are illustrated in Fig.3; Table 1 presents the parameters and the temperature ranges in which these relations were fitted by Eqn.(7). The effective frequencies of the vibrations of the $^{119}$Sn atoms within the anion and of the associated vibrations have been calculated from the $\langle x^2\rangle$ obtained. The frequencies $\nu_{ir}$ are reasonably consistent with the vibrations of species having masses greater than 1000 a.m.u. and weakly linked to one another. They have similar values for all solid halides except complex 2. This is consistent with the crystallographic data, according to which the distances between the atoms in compound *1* are $R(Sn - Cs^+) > 4.5$ Å and $R(F - Cs^+) > 3$ Å and differ little from the distances between the atoms of the $SnCl_3$ and $(CH_3)_4N$ groups in compound *3*.[49-53] The effective intermolecular vibration frequencies decrease in the sequence F > Cl > Br, remaining higher in absolute magnitude than the observed low-frequency components of the spectrum.

**Table 1.** Parameters obtained by fitting Eqn.(7) to the curves in Fig.3.[55]

| Complex* | $T$, K | $10^{18}\langle x^2\rangle_{ia}$, cm$^2$ | $10^{18}\langle x^2\rangle_{ir}$, cm$^2$ | $\alpha_{ia}$, K | $\alpha_{ir}$, K | $\nu_{ia}$, cm$^{-1}$ | $\nu_{ir}$, cm$^{-1}$ |
|---|---|---|---|---|---|---|---|
| *1* | 77–300 | 0.04 | 0.27 | 20 | 100 | 350 | 4.7 |
| *2* | 77–160 | 0.07 | 0.1 | 10 | 100 | 200 | 12.7 |
| *3* | 77–140 | 0.08 | 0.25 | 8 | 120 | 175 | 5.0 |
| *4* | 77–140 | 0.10 | 0.15 | 10 | 120 | 140 | 5.6 |
| *5* | 77–140 | 0.05 | 0.55 | 25 | 100 | 280 | 2.3 |

*The numbers of the complexes correspond to the numbers of the curves in Fig.3.

The calculation,[55] based on the measured force constants of the $SnX_3^-$ anions[57] and the complex $[PdCl_3(SnCl_3)]^{2-}$ [50] as well as the available information about the geometry of the complexes,[19,36,49-53] made it possible to discover a series of important characteristic features of the compounds considered. Firstly, the number of low-frequency (up to 100 cm$^{-1}$) normal vibration modes increases in the sequence F, Cl, Br: 55 cm$^{-1}$ for the F-derivatives, 61, 66, 75, and 82 cm$^{-1}$ for the Cl-derivatives, and 44, 52, 73, 85, 90, 97 cm$^{-1}$ for the Br-derivatives. Secondly, in the presence of bridging F atoms, as in the fragment

$$F_3Sn\diagdown\!\!\diagup F \diagup\!\!\diagdown SnF_3,$$
$$\qquad\quad M$$

the calculated $\langle x^2\rangle$, corresponding to a frequency of 55 cm$^{-1}$, is $11.6 \times 10^{-20}$ cm$^2$, while without a bridging atom, as in the fragment, $F_3Sn–M–SnF_3$, it amounts to $30.6 \times 10^{-20}$ cm$^2$ at a

†The subscripts $f'$ correspond to the temperatures of the measurement (K).

frequency of 74 $cm^{-1}$. Thirdly, the tin atom undergoes the greatest shift in stretching vibrations [$\nu$(SnX) whose observed frequencies decrease in the same sequence of atoms X (524 $cm^{-1}$ for F, 316 $cm^{-1}$ for Cl, and 225 $cm^{-1}$ for Br). The calculated values of $f^*_{ia}$ at $T = 0$, expressed as the product of the $f'_{ia}$ for each of the frequencies quoted above, proved to be 0.64 for the fluorides, 0.58 for the chlorides, and 0.46 for the bromides.

Table 2 presents the values of $f'_{ia}$ and $f'_{ir}$ as well as their temperature variations obtained by Eqns. (3) and (7) and taken from Yurchenko et al.[55] Comparison of the values of $f'_{ia}$ at $T = 0$ with those of the $f^*_{ia}$ listed above shows that the analysis of the vibrations of the metal–tin halide complexes made it possible to estimate correctly their characteristic values of $\langle x^2\rangle_{ia}$ ($T = 0$) and the corresponding $f^*_{ia}$.

The analysis suggested[56] that all the low-frequency vibrational modes, including $\nu$(SnX), contribute effectively to the mechanism of the changes in $f'_{eff}$ in the series of tin(II) halide-containing complexes of transition metals, the increase of the number of such modes from X = F to X = Br and the decrease of $\nu$(SnX) in the same series having the greatest importance. The data of Yurchenko et al.[55] have shown that the values of $f'$ characteristic of the $SnX_3$ ligands occur in the range 77–140 K; they differ little in the series of metals and can be used to analyse the type of tin-containing halide complexes obtained. Table 2 also shows that at $T = 0$ the overall value of $f'_{eff}$ is approximately equally determined by the presence of zero-point vibrations of the tin atom in the anion and associated vibrations of the anion. An increase of temperature, within the limits where Eqn. (7) fitted to the relations shown in Fig. 3 holds, leads to a greater intensification of the internal vibrations of the tin atom, so that along these sections the temperature dependence of $f'$ is determined mainly by the internal properties of the anions. The characteristics of the packing and of the interionic interaction have a greater influence at higher temperatures.

**Table 2.** Temperature dependence of the parameters $f'_{ia}$ and $f'_{ir}$ for the complexes.

| T, K | $f'_{ia}$ | $f'_{ir}$ | T, K | $f'_{ia}$ | $f'_{ir}$ |
|---|---|---|---|---|---|
| $Cs_4[RhSn_4F_{15}(SnF_2\cdot 2H_2O)_2]$ | | | $(Me_4N)_4[OsCl(SnCl_3)_5]$ | | |
| 0 | 0.94 | 0.67 | 0 | 0.89 | 0.69 |
| 77 | 0.79 | 0.63 | 77 | 0.32 | 0.67 |
| 140 | 0.66 | 0.52 | 140 | 0.13 | 0.59 |
| 300 | 0.42 | 0.29 | | | |
| $Cs_3[Pt(SnCl_3)_5]$ | | | $(Me_4N)_4[OsBr(SnBr_3)_5]$ | | |
| 0 | 0.90 | 0.86 | 0 | 0.86 | 0.80 |
| 77 | 0.45 | 0.84 | 77 | 0.32 | 0.79 |
| 140 | 0.26 | 0.78 | 140 | 0.13 | 0.73 |

It was noted above that the establishment of the dependence of the rate and selectivity of a catalytic reaction on the electronic structure of the catalyst atoms was already identified in an earlier review[5] as one of the most important aspects of the application of the Mössbauer effect in catalysis. Unfortunately, so far the study of Skalkina et al.[6] is perhaps the only one where such an attempt was made in relation to a heterogeneous catalytic process. We are unaware of any studies on these lines in relation to homogeneous catalysis. The reason is primarily that, despite the extensive literature describing the catalytic reactions in the presence of $SnCl_3$-containing complexes,[1,18] not even the

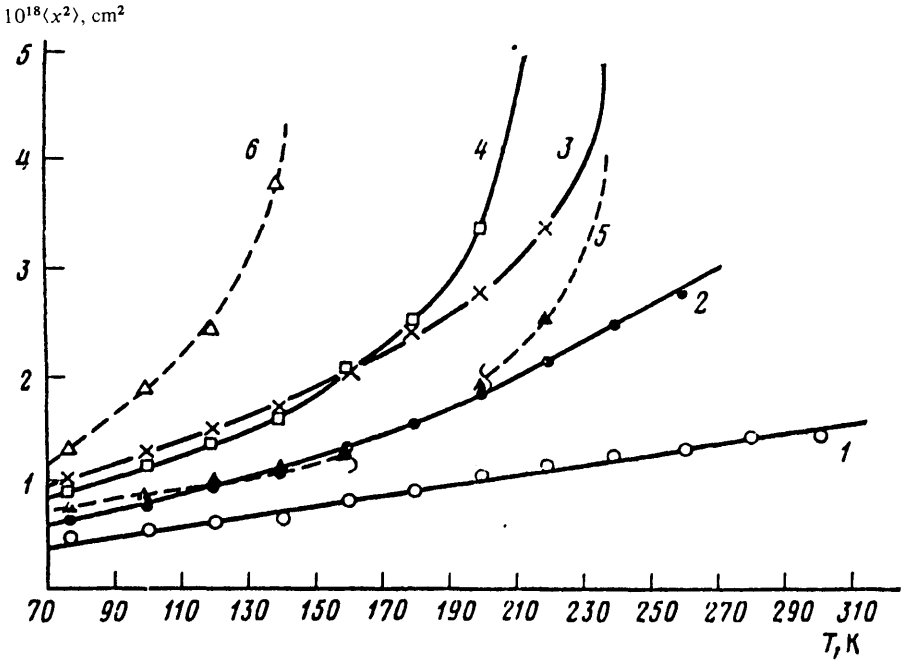



**Figure 3.** Temperature dependence of the effective mean square amplitudes of the shifts of the $^{119}Sn$ atoms in tin halide catalysts: *1*) $Cs_4\{Rh(Sn_4F_{15})[SnF_2(H_2O)_2]_2\}.4H_2O$; *2*) $Cs_3[Pt(SnCl_3)_5]$; *3*) $(Me_4N)_4[OsCl(SnCl_3)_5]$; *4*) $(Me_4N)_4[OsBr(SnBr_3)_5]$; *5*) $[RuSn_3F_{18}]^{4-}$ solution in 3 M HF (0.015 M); *6*) $[Pd(SnCl_3)_5]^{3-}$ solution in 3 M HCl (0.032 M).

composition of the complex functioning as the true catalyst has been elucidated in any of the studies except those in Refs.1, 18, 58. At the same time, other causes limiting the extensive possibilities for the determination of the electronic structure of the tin atoms in tin-containing homogeneous complexes provided by the analysis of Mössbauer spectroscopic parameters such as $\delta$ and $\Delta$ have also been noted.[18] The first parameter is related to the spherical symmetry of the electron density distribution around the nucleus of the tin atom:[14]

$$\delta = C\frac{\Delta r}{r}\Delta|\psi_{ns}|^2 , \qquad (8)$$

where $C$ is a constant characterising the Mössbauer nucleus, $\Delta r$ the difference between the radii of the nuclei in the ground and excited states, $r$ the radius of the nucleus in the ground state, and $\Delta|\psi_{ns}|^2$ the difference between the electron densities generated by the $ns$ electrons on the nuclei of the absorber and the source of $\gamma$-quanta.

Since the change in the population of the valence 5$s$ atomic orbitals (AO) of tin makes the main contribution to $\Delta|\psi_{ns}|^2$, the reason for the interest in the direct estimation of the latter from $\delta$ and conversely is fairly obvious.[13,14] However, two difficulties arose in the determination of the above quantities: the lack of an exact value of $\Delta r/r$ and the fairly considerable scatter in the estimates of the shielding influence of the 5$s$, 5$p$, and 5$d$ electrons on the 5$s$ electron of the tin atom.[18] The necessity to determine the exact value of $\Delta r/r$ has been discussed in detail.[14] However, hitherto there exists no unanimous view concerning the estimation of $\Delta r/r$, which has been well illustrated in the paper by Vertes et al.[16], where values of $\Delta r/r$ ranging from $0.73\times10^{-4}$ to $2.05\times10^{-4}$ are presented even on the basis of the very latest data.

Allowance for the shielding of the 5$s$ electron by the 5$s$, 5$d$, and 5$p$ electrons in the first studies on this question led to different estimates of its extent.[59,60] Subsequently numerous expressions relating the measured values of $\delta$ to the population of the 5$s$, 5$p$, and 5$d$ AO of tin in compounds were proposed[61-63] but none of them is sufficiently universal.[18] This situation is clearly demonstrated by Table 3, which lists the values of $\delta$ for tin species widely used in catalysis–$SnCl_4$ and $SnCl_3^-$; these values were calculated using the populations of the 5$s$ (S) and 5$p$ (P) AO obtained[17,18,64] from the three formulae proposed by Antoncik[61] and also from the formulae quoted by Gol'danskii and Makarov[59] and by Flin.[60] Evidently, within the framework of any of the approximations for the estimation of $S$ and $P$ for the same compound, the values of $\delta$ differ by a factor of 1.5–3. At the same time the data in Table 3 show that the parametrisation of the semi-empirical LCAO-MO method yields differences of the same order of magnitude. Whereas calculation for $SnCl_4$ yields as a rule values of $\delta$ which are much too high, within the framework of the same LCAO-MO approximation those obtained for $SnCl_3^-$ are too low. Here one must note that the dependences of $\delta$ on $S$, $P$, and $D$ have been obtained using different values of $\Delta r/r$. Thus Gol'danskii and Makarov[59] adopted $3.3\times10^{-4}$, while Antoncik[61] adopted $0.92\times10^{-4}$.

Thus neither the parametrisation of the LCAO-MO methods for tin compounds nor the estimation of the populations of the 5s, 5p, and 5d AO for the tin atom in such compounds on the basis of the measured $\delta$ are possible without refining and standardising the values of $\Delta r/r$ and the shielding parameters. However, within the framework of a narrow range of compounds, any of the proposed dependences of $\delta$ on $S$, $P$, and $D$ reproduce satisfactorily the principal characteristics of the changes in $\Delta|\psi_{5s}|^2$. Thus the populations of the 5$s$ and 5$p$ AO of the tin atom in $SnCl_3^-$ and the complexes obtained in terms of the Mulliken–Wolfsberg–Helmholtz (MWH) approximation[51] yield the following values of $\delta$ estimated by the formula quoted by Herber et al.[63]: 3.38 mm $s^{-1}$ for $SnCl_3^-$, 2.8 mm $s^{-1}$ for $[PtCl_3(SnCl_3)]^{2-}$, and 2.96 mm $s^{-1}$ for $[PtCl_2(SnCl_3)_2]^{2-}$. These results show that the MWH approximation can reflect fairly roughly the charge distribution in the complex but the principal features (the decrease of $\Delta|\psi_{5s}|^2$ for the tin atom on coordination and its greatest decrease for the complex with the M:Sn = 1:1 ratio) are reproduced correctly.[51]

Table 3. The parameters $\delta$ obtained in calculations of the populations of the 5$s$ and 5$p$ AO of the tin atom in terms of the LCAO-MO approximations.

| Method of calculation of $S$ and $P$ | $\delta$*($SnCl_4$) | | | | | $\delta$*($SnCl_3^-$) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1**–[63] | 2–[63] | 3–[63] | [59] | [60] | 1–[63] | 2–[63] | 3–[63] | [59] | [60] |
| CNDO (Ref.64) | 1.12 | 2.2 | 0.74 | 1.68 | 1.95 | — | — | — | — | — |
| CNDO-Cl (Refs.17, 18) | 2.05 | 3.44 | 2.16 | 2.63 | 3.03 | 3.19 | 5.27 | 3.31 | 2.62 | 4.24 |
| MWH (Ref.18) | 0.99 | 2.1 | 0.82 | 1.60 | 1.80 | 2.33 | 2.18 | 2.40 | 1.92 | 2.83 |

*The parameters $\delta$ are given relative to $Ba^{119}SnO_3$: $\delta_e(SnCl_4) = 0.85$ mm $s^{-1}$;[65] $\delta_e(SnCl_3^-) = 3.64$ mm $s^{-1}$.[28]
**The numerals 1, 2, and 3 refer to the dependences of $\delta$ on $S$ and $P$ taken from Ref. 63 (in sequence).

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

Direct correlations between $\delta_e$ and $\Delta|\psi_{5s}|^2$ have been used in a number of studies and satisfactory results have been obtained.[16,64,66] They show that, at least in a series of related compounds, it is possible to interpret the differences in $\delta$ as a consequence of the changes in the population of the 5$s$ AO of the tin atom. This information is important for the study of the mutual influence of the ligands in the complex and also for the determination of the AO involved in the interaction of the homogeneous catalyst with the molecule being activated and in the change of the properties of the catalyst under various conditions.

In discussing the possibility of using the Mössbauer parameters to characterise the features of the electronic structure of tin halide complexes, it is essential to consider the problem of the use for this purpose of quadrupole splitting in a number of investigations. We have

$$\Delta = \frac{e^2qQ}{2}\left(1+\frac{\eta^2}{3}\right)^{1/2} , \qquad (9)$$

where $eq$ is the electric field gradient (EFG) at the nucleus in the direction of the emission of $\gamma$-quanta (the $z$ axis), $Q$ the quadrupole moment of the nucleus characterising the deviation of the distribution of the average charge density on the nucleus from spherical symmetry and $\eta = (q_{xx}-q_{yy})/.q_{zz}$ the asymmetry parameter.[13] The gradient $eq$ is determined for tin mainly by the population of the $5p_z$ AO. The expressions for the dependences of the EFG in the direction of the $x$, $y$, and $z$ axes ($q_{xx}$, $q_{yy}$, and $q_{zz}$ respectively) in terms of the populations of the $p_x$, $p_y$, and $p_z$ AO have been published.[13] Thus $\Delta$ can serve as a measure of the uniformity of the population of the $5p_{x,y,z}$ AO of the tin atom and is a parameter sensitive to the structure of the immediate environment of the atom.

The authors of one of the first studies[30] on the Mössbauer spectra of $SnCl_3$-containing complexes explained the increase of $\Delta$ on passing from salts of the $SnCl_3^-$ anion to complexes by electron transfer from the metal atom to the $\pi^*$ orbital of $SnCl_3$, incorporating the $5p_{x,\,y}$ AO of the tin atom with the simultaneous decrease of the number of electrons in the $5p_z$ AO owing to the formation of a $\sigma$-bond, which intensifies the non-equivalence of the populations of the $p$ AO of the tin atom. Subsequently the chage in $\Delta$ was regarded in certain studies, for example, those of Antonov and co-workers,[67,68] as a direct measure of the $\pi$-acceptor properties of the ligand $SnX_3$ (X = Cl or Br), i.e. a measure of the increase of the population of the $5p_{x,\,y}$ AO of the tin atom in the ligand.

The change in the distribution of electron density in the $SnX_3^-$ anions on $\sigma$-donor transfer of the electron pair from the highest occupied MO has been analysed.[17,18,34] The data presented show that such transfer does indeed entail a marked population decrease of the $5p_z$ AO of the tin atom, which induces the appearance of a negative $q_{zz}$, which increases in absolute magnitude from F- to I-derivatives. According to Yurchenko's estimate,[18] this effect leads to the following increments in $\Delta$ for the $SnX_3$ ligand compared with the $SnX_3^-$ ion: 0.83 mm $s^{-1}$ for $SnF_3$, 1.43 mm $s^{-1}$ for $SnCl_3$, 1.70 mm $s^{-1}$ for $SnBr_3$, and 2 mm $s^{-1}$ for $SnI_3$. The changes in $\Delta$ in the series of X observed for the $SnX_3$-containing complexes agree with these estimates, although they are somewhat lower in absolute magnitude.[50,51] This shows that the $\Delta$ cannot be used to estimate the $\pi$-acceptor properties of the ligands $SnX_3$ without taking into account the contribution to the changes in the population of the $5p_\sigma$ AO of the tin atom as a consequence of the $\sigma$-donor transfer $X_3Sn \rightarrow M$.

The values of $\delta$ and $\Delta$ for the $SnX_3$-containing complexes have been published mainly in Refs. 1, 18, 19, 29, and 31–36.

The inverse proportionality between $\delta$ and $\Delta$ can be usually traced in tin(II) compounds with donor–acceptor bonds.[13] In the case of a purely ionic bond between tin(II) and its environment (the $5s^25p^0$ configuration), we should have $\Delta = 0$ and an increase of the population of the $5p$ shell should lead to $\Delta \neq 0$. According to Shpinel's estimate,[13] one unbalanced $p$ electron in the $z$ axis direction should then give rise to $\Delta = 3$ mm $s^{-1}$. However, for coordinated $SnX_3$ ligands such a relation between $\delta$ and $\Delta$ has not been observed, as for the tin compounds mentioned above; this serves as yet another piece of evidence demonstrating the complexity of the redistribution of the population of the $5p_{x,\,y,\,z}$ AO of the tin atom on coordination of the $SnX_3$ groups.

Thus it is at present impossible to predict beforehand which precise changes in $\delta$ and $\Delta$ will be undergone by particular tin(II) compounds and the structural identification of the latter can be achieved in only one way—by determining the boundary values and other characteristics of the Mössbauer parameters by studying compounds of different types but with known structures established by X-ray diffraction, which has been partly done in two investigations.[17,18]

## 2. Heterogeneous Systems

Two applications of tin-containing compounds in heterogeneous catalysis have now arisen: (1) the immobilisation of $SnCl_3$-containing transition metal complexes on the surfaces of carriers;[18] (2) the deposition on the surfaces of carriers of either these complexes or of tin-containing compounds and transition metal compounds (usually platinum) separately with subsequent high-temperature reduction until M–Sn alloys are formed.[3] In both cases a series of specific complications arise in the application of the Mössbauer effect for the identification of tin compounds on the surfaces of carriers and for the characterisation of their state.

Thus it has been shown[69] that some of the tin compounds formed on the $ZnAl_2O_4$ surface are readily oxidised by oxygen, which requires the preparation of the specimens and the recording of the spectra under conditions where access of air can be ruled out. Flat sealed bulbs made of thin molybdenum glass have proved very useful for this purpose.[70] In preparing such bulbs, one must keep their flat sides parallel and the distance between them should ensure an effective thickness of the specimen $C_a$ less than unity.[13] Such cells have been used[26,27,54,69–72] to record the Mössbauer effect in the temperature range 77–300 K.

When $SnCl_3$-containing complexes and other tin(II) compounds, for example $SnCl_2$, are fixed on the carrier, the Mössbauer parameters change appreciably;[26,27,54,73] there is a particularly pronounced alteration of $f'$. Fig. 4 illustrates the changes in $f'$ for different tin(II) compounds when they are deposited on $\gamma$-$Al_2O_3$.[54,55,73] Since the tin(II) compounds were deposited by impregnating the carrier with their solutions in organic solvents, after the removal of the solvent and drying of the specimen, the tin(II) compounds were present on the specimen surface in the form of molecules linked to specific centres on the carrier.[74] In this case the conclusion reached by Yurchenko et al.[55] that an increase of $f'$ (Fig. 4) implies a strong chemical interaction of the $SnCl_3$ ligands in the complex or of the $SnCl_2$ molecules with the surface as a consequence of the partial hydrolysis of the Sn–Cl bond by the acid OH groups,[55] i.e.

$$\left|-OH + Cl_2Sn{-}ML_n \rightarrow \right| -O{-}SnCl_2{-}ML_n + HCl\,, \qquad (10)$$

can be used to explain the changes in $f'$.

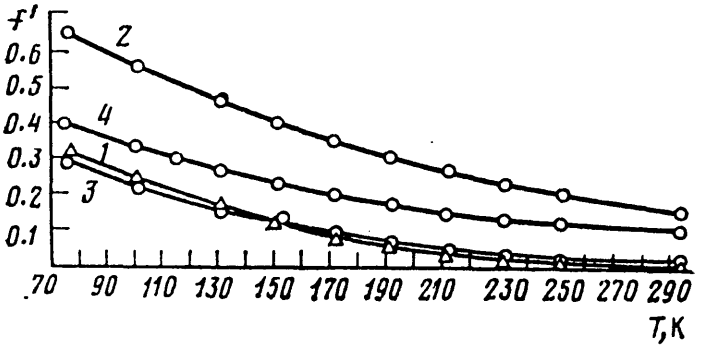



**Figure 4.** Temperature dependence of $f'$: *1*) $SnCl_2.2H_2O$; *2*) $SnCl_2$ on $\gamma$-$Al_2O_3$; *3*) $(Et_4N)_2[PtCl_2(SnCl_3)_2]$; *4*) $[PtCl_2(SnCl_3)_2]^{2-}$ on the surface of $\gamma$-$Al_2O_3$.

After treating these specimens under the reaction conditions ($H_2$ atmosphere, temperature 773 K), a set of tin compounds are as a rule formed on the surface, giving rise to very complex overall spectra (Fig. 5, curves *1*, *2*, *5*, and *6*). The identification of individual tin compounds on the catalyst surface requires in such cases the resolution of

the complex contour of the Mössbauer spectrum into individual components. In this case the problem is much more complex than in the analysis of individual Lorentzian components in the spectra of clusters (cf. Fig. 1). Similar complex spectra are observed when different carriers and when different methods of preparation of the catalysts are used.[10,69–72,75–77]

As each of the tin compounds identified can be chemically bound to the surface or can exist in a finely dispersed state, where most of the Mössbauer atoms do not interact with the surface and compounds of this kind do not as a rule exist in an individual state, some uncertainty arises about the selection of the parameters ($\delta$, $\Delta$, and $f'$) of the individual components of the spectrum. Two approaches arose in the consideration of the question of the permissible variation of the Mössbauer parameters of the individual components. In the first, the values of $\delta$ and $\Delta$ for the individual components remain close to those for the individual substances in the massive state. Clearly such resolution is closer to the true one the coarser the dispersion of the test substances and the weaker their interaction with the surface. If such resolution cannot be carried out, the parameters can be altered somewhat, for example, $\Delta$ can be increased, but within the limits of the values encountered for individual systems. The parameter $f'$ is not then measured.[10,70–72]

The second approach consists in the investigation of the changes in $\delta$, $\Delta$, and $f'$ when various tin compounds, whose formation may be expected, interact with the surface, and in the resolution of the overall spectrum into components with parameters corresponding to the interaction of the individual compounds with the surface. It is then implied that the compounds do not interact with one another or that this interaction is not reflected in the Mössbauer

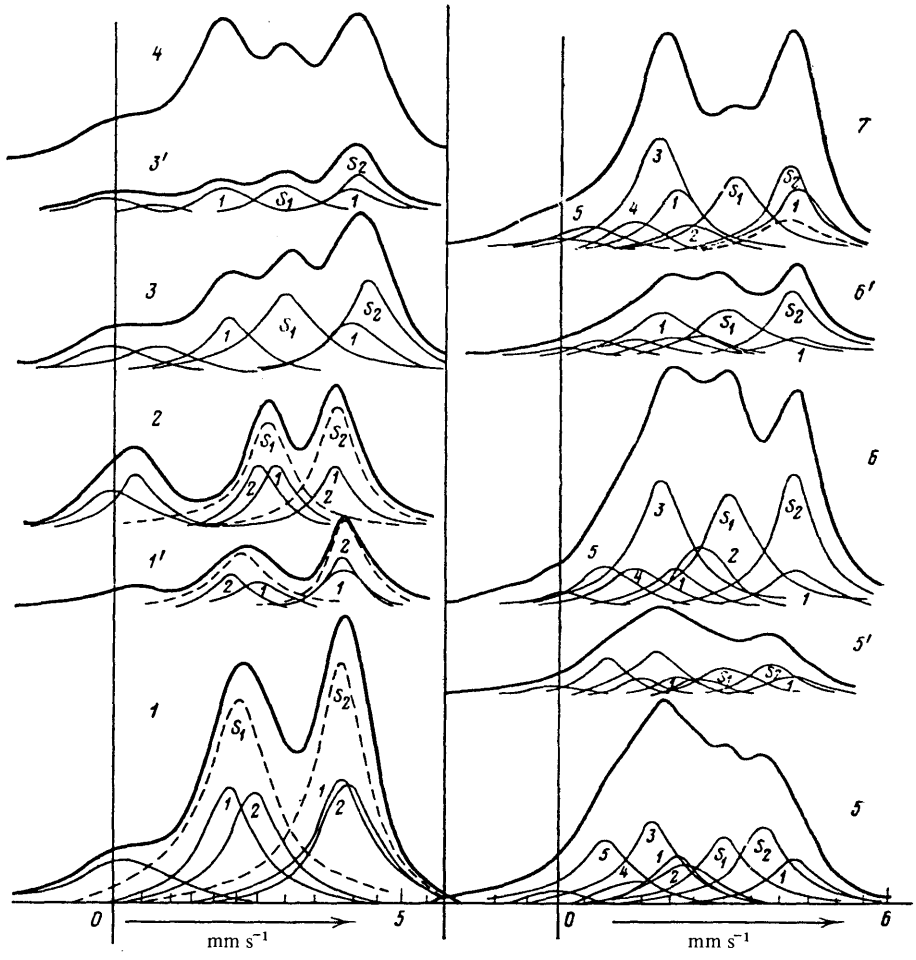



**Figure 5.** Mössbauer spectra resolved into individual components on an SK-2 synthesiser: *1*) and *1'*) $SnCl_2$ on $\gamma$-$Al_2O_3$; *2*) $SnCl_2$ on $\gamma$-$Al_2O_3$ chlorinated beforehand [$\gamma$-$Al_2O_3$(Cl)]; *3*) and *3'*) specimen 2 reduced in a stream of $H_2$ (773 K); *4*) overall spectrum of specimen 3 and Pt–Sn alloys; *5*) and *5'*) Pt–Sn/$\gamma$-$Al_2O_3$; *6*), *6'*), and *7*) Pt–Sn/$\gamma$-$Al_2O_3$(Cl); specimens 5 and 6 were obtained by depositing the complex $[PtCl_2(SnCl_3)_2]^{2-}$ and were reduced in a stream of $H_2$; specimen 7 was obtained after repeated oxidation-reduction cycles; spectra *1*–*7* were recorded at 77 K and spectra *1'*–*6'* at 295 K.

parameters. This approach has been used by Yurchenko and Kuznetsov[73]# and, to a limited extent, without analysis of the values of $f'$, by Gray and Fahra[75] and Berndt et al.[76] However, in this case too it is frequently impossible to achieve a unique resolution and one must consider all the alternative interpretations of the spectra. Such data have been reported.[73,76]

A major complication in the selection of the initial values of $\delta$, $\Delta$, and $f'$ for the resolutions arises from the influence of the degree of dispersion of the compounds on the parameters of the Mössbauer spectra. Analysis of the characteristic features of the Mössbauer spectra of molecular crystals has shown[18,55,73] that the differences between the electronic structures and the dynamics of the movement of the tin atom in a complex molecule are determined predominantly by the molecular structure. Thus the transfer of a molecule from the crystal to the solution hardly influences $\delta$ and $\Delta$ and entails merely a decrease of $f'$. The physical adsorption of tin-containing molecules on the carrier surface should therefore not alter $\delta$ and $\Delta$ either. The observed[26,27,54,73] changes in $\delta$ and $\Delta$ on deposition of tin compounds on a carrier are in fact associated with the partial alteration of the chemical composition of the molecule, illustrated in Scheme 10, i.e. with the partial replacement of the Cl atom by O in the coordination sphere of tin. One can also assume that tin(IV) compounds ($SnO_2$, $SnCl_4$, etc.) and tin(II) compounds ($SnCl_2$, $SnCl_2.nH_2O$, SnOHCl, SnO) have (when their molecular composition is retained) values of $\delta$ and $\Delta$ on the carrier surface close to those characteristic of the individual compounds.

The changes in $\delta$ and $\Delta$ owing to the possible chemical reactions on the surface can be modelled by investigating the parameters of the spectra of the pure substances analogous to the products of such reactions. The situation is more complex as regards the parameters of the phases with closer packing such as β-tin and Pt–Sn alloys. For example, the study of the dependence of $f'$ on the degree of dispersion of β-tin showed that $f'$ for the surface atoms diminishes markedly.[78] Specimens with particle sizes ranging from 1500 to 200 Å have been investigated,[78] but, from the standpoint of catalysis, even the latter are coarsely dispersed specimens. Information about the changes in $f'$ when the particle size is varied from 200 to 10 Å is essential for catalysis. This problem has not been studied rigorously; the main difficulty in this instance involves the preparation of highly dispersed specimens with a uniform distribution of particles with respect to size.

It follows from general considerations (see, for example, Suzdalev[15]) that the frequency of the phonon spectrum increases for a very small particle size and this can actually lead to an increase of $f'$ for the particles. The transition to clusters (particle size 10–30 Å) should alter not only $f'$ but also the parameters $\delta$ and $\Delta$ of the Mössbauer atom. Such finely dispersed formations should appear only as a consequence of an intense interaction with the surface and there is no reason to regard them as finely dispersed particles having the properties of the phase present in the coarsely dispersed state. It is more reasonable to regard them as new compounds incorporating carrier atoms in their composition. Such a system ($Pt–Sn/SiO_2$) has been investigated;[70] the size of particles containing only platinum and tin was $10 \pm 3$ Å and the Mössbauer effect due to the tin atoms was manifested by a doublet with $\delta = 1.43$ mm $s^{-1}$ and $\Delta = 2.32$ mm $s^{-1}$.

Thus the final result of the fragmentation of the Pt–Sn alloy particles on the carrier is the formation of clusters, in which the platinum atoms interact with the tin bound to the surface. The parameters $\delta$ and $\Delta$ of such tin atoms then assume values approaching $\delta$ and $\Delta$ for the tin(II) complexes with transition metals. At least under the conditions of such dispersion, there is no possibility of a very large increase in $\Delta$, unaccompanied by a significant change in $\delta$, which has been postulated[77] in the resolution of the Mössbauer spectrum of the $Pt–Sn/Al_2O_3$ catalyst.

A finely dispersed phase of the Pt–Sn alloy, whose parameter $\delta$ varies within the limits 1.85–2.13 mm $s^{-1}$ ($\delta = 1.97$ mm $s^{-1}$ for the massive alloy) and $\Delta$ varies from 0.3 to 5.26 mm $s^{-1}$, has been identified[71] on specimens with different platinum contents. The last value should correspond to a difference between the populations of the $5p_\sigma$ and $5p_\pi$ AO of the tin atom of 1.75 electrons. Such a difference has not been observed even for the $SnB_9C_2H_4$ structure, where the coordination of the tin atom models effectively a purely surface disposition on the carrier;[62] it is even more unrealistic for the coordination of the tin atom to the symmetrically arranged electron-saturated Pt(0).[79]

The differences between the permissible variations in $\delta$ and $\Delta$, which can be identified on the surfaces of compounds, have been one of the causes of the discrepancies in the descriptions of the state of tin(IV) and tin(II) and of the types of alloys on the surface of $\gamma$-$Al_2O_3$ in the studies of Bacaud and co-workers,[10,77] on the one hand, and Yurchenko and co-workers,[72,73] on the other. In our view, the initial resolution of the spectra for fixed values of $\delta$ and $\Delta$ for the individual components of the Mössbauer spectrum, corresponding to individual tin compounds, is methodologically correct. When $\delta$ and $\Delta$ are varied in an arbitrary manner, the resolution ceases to be in any way definite. Simultaneously with this procedure, one should deposit all the necessary individual substances on the carrier, the specimen should be treated under the same conditions as the catalyst, and the variation of $\delta$, $\Delta$, and $f'$ should be investigated, and then the parameters of the individual components obtained on resolution of the spectra of the catalyst should be appropriately corrected. It has been shown[55,73] that in many cases information of decisive importance for the identification of the state of the Mössbauer atom on the surface is provided by the analysis of the temperature variation of $f'$. The ratio $f'_{77}/f'_{295}$ can be used as the simplest and most convenient parameter of the dependence of $f'$ on $T$.

In view of the special sensitivity of the parameter $f'$ to the type of the tin-containing compounds, investigation of the specimens at least at 77 and 295 K and the maintanence of the ratios $f'_{77}/f'_{295}$ for all the components on resolution of the spectrum within specific characteristic limits make such resolutions significantly more rigorous as regards the identification of the number and types of different tin-containing formations on the surface. The range of variation of $\delta$ and $\Delta$ as well as $f'_{77}/f'_{295}$ for the tin compounds identified on the $\gamma$-$Al_2O_3$ surface has been indicated by Yurchenko and Kuznetsov[73]§ and Yurchenko.[18]

The ratios $f'_{77}/f'_{295}$ for different tin(II) and tin(IV) halides, oxides, and sulphides,[80] for massive PtSn and $PtSn_2$ [81,82] alloys, and for $SnX_3$-containing complexes[55] have been published.

#The analysis of the Mössbauer spectra of such systems is discussed in detail in the paper by V.I.Kuznetsov, A.S.Belyi, and E.N.Yurchenko, J.Catal (in the Press).

§See the previous footnote concerning the report of Yurchenko and Kuznetsov.[73]

## III. THE PROPERTIES OF TIN-CONTAINING CATALYSTS

### 1. Homogeneous Catalysts

Matvienko[1] gave a systematic account of most of the studies published up to 1978 where platinum metal compounds with the $SnCl_3$ ligand have been used as catalysts of the reactions of various organic substances. In the same communication and also in Yurchenko's thesis,[18] it is noted that the state of the $SnCl_3$-containing complexes in the reaction medium has not been established in any of these catalysts. Mössbauer spectroscopy has not been used for such purposes.

Later, several communications, also dealing with the catalytic properties of $SnCl_3$-containing complexes, were published. It has been reported[83] that, in the presence of the complex $Rh(PPh_3)_3.(SnX_3)$ (X = Cl or Br), catalytic hydrogenation of olefins takes place. The authors concluded that an unidentified hydride complex exhibits a hydrogenating activity. It has been found[84] that the rhodium(I) complex $[Rh_2Cl_2(SnCl_3)_4]^{4-}$ is active in the isomerisation of olefins, but it has been concluded[67] that the complex should be regarded as a rhodium(III) compound, apparently having the composition $[RhCl_4(SnCl_3)_2]^{3-}$.[85] Antonov et al.[67] investigated $SnCl_3$-containing rhodium(III) compounds ranging from $[Rh(SnCl_3)_2Cl_4]^{3-}$ to $[Rh(SnCl_3)_5Cl]^{3-}$ (by the Mössbauer method), but their state in the presence of olefins was not characterised. Borunova et al.[86] examined the catalytic properties of the complexes $[MX(SnX_3)_5]^{n-}$ (M = Pt, Rh, Ir, Ru, or Os, X = Cl or Br) in the hydrogenation and isomerisation of olefins. The initial compounds were characterised by Mössbauer spectroscopy mainly in the study of Yurchenko et al.[32] However, in this case the authors concluded that the complex undergoes a change in composition in solution and that hydride forms are active, for example, in isomerisation, but these two were not identified or investigated by Mössbauer spectroscopy either. This applies likewise to the complex $[Ru(PPh_3)_2.(SnCl_3)Cl]$, in the presence of which catalytic hydrogenation of olefins takes place.[87]

Thus only the initial $SnCl_3$-containing complexes, forming the intrinsic catalytically active species under the conditions of the catalysis, have been characterised by the Mössbauer method in the studies enumerated above. The lack of Mössbauer spectroscopic data for the intrinsic catalytically active forms precludes the analysis of the relation between their $\delta$ and $\Delta$, on the one hand, and the catalytic activity of such compounds, on the other. This situation can be avoided perhaps only in the case of the chlorocarbonyltin complexes $[IrClCO(SnCl_3)_2]^{2-}$ (I), $[RhClCO(SnCl_3)_2]^{2-}$ (II), $[PtCl_2CO(SnCl_3)]^{-}$ (III), and $[IrCl_3CO(SnCl_3)_2]^{2-}$ (IV), which have been investigated by a series of physical methods, including Mössbauer spectroscopy.[34] It has been shown[1,18] that these complexes are in fact the catalytically active forms in the homogeneous dehydrogenation of HCOOH. In this connection, one may note that for the first three complexes in which the transition metal has the $d^8$ configuration, the reaction rate constants $k$, $\delta$, and $\Delta$ vary in parallel: $3\times10^{-3}$ $s^{-1}$, 1.73 mm $s^{-1}$, and 2.15 mm $s^{-1}$ for compound (I), $1.2\times10^{-4}$ $s^{-1}$, 1.64 mm $s^{-1}$, and 1.92 mm $s^{-1}$ for compound (II), and $1.5\times10^{-5}$ $s^{-1}$, 1.58 mm $s^{-1}$, and 1.60 mm $s^{-1}$ for compound (III).[1] On passing to the iridium(III) compound with the $d^6$ configuration, $k$ diminishes appreciably ($4.5\times10^{-5}$ $s^{-1}$), but $\delta$ and $\Delta$ for the Sn atom in the $SnCl_3$ ligands in this complex increase (1.83 and 2.08 mm $s^{-1}$ respectively).

Thus the direct relation between the Mössbauer parameters and the rate constants for catalytic reactions in such systems can hardly be regarded as adequately universal. Analysis of the mechanism of the catalytic dehydrogenation of HCOOH, proposed by Yurchenko and Anikeenko,[88] and also valid for $SnCl_3$-containing complexes,[1] showed that the properties of this ligand influence two stages of the process: the substitution of one $SnCl_3$ ligand by $HCOO^-$ and the rate-limiting stage involving the rupture of the H—C bond. The role of the intrinsic properties of the ligand in cases where the central atom of the complex is Ir(I) or Ir(III) is indeed found to be different.[18,88]

The first tin-containing zerovalent palladium clusters which have been obtained and characterised[21] proved to be catalytically active in the conversion of olefins into the cyclic esters of polyhydric alcohols (anhydroalditols).[1] In this case Mössbauer study of the clusters made it possible to refine their composition.[21] It was mentioned above why the parameters $f'$ were used for this purpose (Fig. 1). For all the palladium clusters, the values of $\delta$ and $\Delta$ for the individual Lorentzian components were analysed together with $f'$. In particular, it was shown that the observed $\delta$ for the second type of tin(II)-containing ligand satisfy the condition of a linear decrease of the 5*s* electron density in the sequence $PdSnCl_3 > Pd_2SnCl_2 > Pd_3SnCl > Pd_4Sn$.[21] Anions having the composition $[Pd_2(SnCl_2)_2(SnCl_3)_4]^{2-}$, $[Pd_3(SnCl)_2.(SnCl_3)_6]^{4-}$, and $[Pd_4(Sn)_2(SnCl_3)_8]^{4-}$ have been identified.[1,21] A communication has been published recently[89] whose authors, repeating Matvienko's study,[1] found other compositions of clusters containing four palladium atoms: $[Pd_4(SnCl_2)_2(SnCl_3)_8]^{5-}$ and $[Pd_4(SnCl_2)_2(SnCl_3)_4Cl_2]^{6-}$. The communication[89] contains no arguments justifying this difference nor a discussion of the structure of the clusters obtained. The measured parameters of the Mössbauer spectra of the above compounds, which differ from the parameters quoted for clusters by Elizarova et al.[21], do not prove that Antonov et al.[89] obtained compounds having a composition different from those found by Matvienko[1] because $\delta$ and $\Delta$ for familiar palladium(II) complexes, in particular $[Pd(SnCl_3)_5]^{3-}$, obtained by Antonov et al.[89] differ from those found in other studies[1,21,33,34] by an amount greatly exceeding the experimental error.

The Mössbauer method occupies a notable place in studies where questions concerning the formation and stability of $SnCl_3$-containing complexes and the mutual influence of the ligands in them, which are important for homogeneous catalysis, are investigated. The formation of such complexes in methanolic and aqueous HCl solution was first investigated by the Mössbauer method in the $H_2PtCl_6.H_2O$–$SnCl_2.2H_2O$ system.[24] The authors observed the reduction of platinum(IV) to platinum(II) by bivalent tin, demonstrated the coordination of the platinum(II) atom to $SnCl_3$, and attempted to determine the composition and stability of the complex formed in solution from saturation curves. Later it was shown[25] that the inflections in the saturation curves for such systems do not yield reliable information about the composition of the complexes formed. In the given study of complex formation in the system comprising $K_2PtCl_4$ in 0.5 M HCl solution and $SnCl_2.2H_2O$, the composition of the dominant complexes was determined from the characteristic values of $\delta$ and $\Delta$ for the individual components after the resolution of the spectrum into the Lorentzian doublets. Two complexes with the Pt : Sn = 1 : 2 ratio and a 1 : 5 complex were identified. It was observed that in solution tin(IV) appears rapidly for low Pt : Sn ratios (1 : 1–1 : 2), which might have indicated the reduction of platinum(II) to the zerovalent state with formation of the $[Pt_3Sn_8Cl_{20}]^{4-}$ state.[1]

Yurchenko et al.[26] investigated analogously the formation of complexes between $RuCl_6^{2-}$ and $SnCl_2$ in aqueous 3 M HCl

solution. The composition of the complex was also not determined from the point of inflection in the relation between the concentration of the tin bound in the complex and the Sn:Ru ratio in the system, but was found from the parameters $\delta$ and $\Delta$, which were compared with their values for the individual species $[RuCl(SnCl_3)_5]^{4-}$. In view of their identity over the entire range of Sn:Ru ratios, it was concluded that only this complex is formed under the conditions considered.

The complex formation reaction between $IrCl_6^{3-}$ and $SnCl_2$ in aqueous 3 M HCl solution has been investigated by Antonov et al.[90] who obtained the same Mössbauer parameters of the complex $[IrCl(SnCl_3)_5]^{3-}$ as those discussed previously[34] and this finding, and not the Sn:Ir ratios at which inflections were observed on the saturation curves, confirms the validity of the determination of the composition of this complex in solution.

Thus the saturation curves for the formation of complexes of $SnCl_3$ with a transition metal, plotted from data obtained by any of the physical methods, do not constitute a reliable means of determining the composition of the complex and, when Mössbauer spectroscopy is used for this purpose, it is essential to compare the parameters of the differentiated doublets with those of the spectra of the individual compounds. It has been shown[33] that the variation of the nature of the cations in the latter affects to some extent only the magnitude of $\Delta$, which makes it possible to compare $\delta$ and $\Delta$ for complex anions in solutions with the corresponding parameters of their salts. In view of the foregoing, the identification of the complex $[IrCl_4(SnCl_3)_2]^{3-}$ by Antonov et al.[90] appears controversial.

The investigation of the state of the $SnCl_3$-containing complexes in solution was subsequently continued.[21,26,27] Analysis of frozen $PdCl_4^{2-}$ and $SnCl_2$ solutions in methanol and in aqueous 2.4 M HCl solution, after standing for a long time in an inert atmosphere, confirmed that the rapid process involving the formation of palladium(II) complexes with the $SnCl_3$ ligand is accompanied by the reduction of palladium(II) to zerovalent palladium, which forms, at a specific instant, clusters whose composition was discussed above.

The complex formation reaction between $H_2PtCl_6$ and $SnCl_2$ in aqueous acetone solution containing HCl has been studied[27] and the dynamics of the behaviour of two types of complexes, namely $[PtCl_3(SnCl_3)]^{2-}$ (A) and $[PtCl_2.(SnCl_3)_2]^{2-}$ (B) was followed. It was found that, apart from the reduction of platinum(IV) to platinum(II) and the formation of platinum complexes indicated above, there is a slow increase of the amount of tin(IV) in the system. After a time, the complex (B) was converted into the complex (A) and the platinum in the latter was reduced to the zerovalent state.¶ The formation of a platinum(II) chloride complex with $SnCl_2.2H_2O$ in isopropyl alcohol has been investigated[21] by Mössbauer spectroscopy. Two types of complexes, namely $[Pt(SnCl_3)_5]^{3-}$ and $[PtCl_2(SnCl_3)_2]^{2-}$, were found. Depending on the HCl content, they can be interconverted. The platinum(II) complexes of the first type are stabilised at high HCl concentrations. After a time, the successive transformation $[Pt(SnCl_3)_5]^{3-} \rightarrow [PtCl_2(SnCl_3)_2]^{2-} \rightarrow [PtCl_3.(SnCl_3)]^{2-} \rightarrow$ Pt–Sn alloy takes place. The alloy is present in solution in an ultradispersed state in a mixture with the last two complexes.

¶Unfortunately, as a result of an error by the Publishing House, in the issue of the journal React.Kinet. Catal.Letters containing Refs.26 and 27, Fig.1 from Ref.26 and Fig.2 from Ref.27 were transposed. Readers are requested to take this fact into account.

Thus Mössbauer studies of the state of the platinum and palladium complexes of the $SnCl_3$ ligand in various solutions revealed their important feature—their tendency towards slow inner-sphere conversion by an oxidation-reduction reaction into clusters of zerovalent metals or into intermetallic compounds.

We shall consider briefly the results of the application of Mössbauer spectroscopy to the study of the mutual influence of ligands. It has been shown[17,34] that a combination of Mössbauer spectroscopy, NMR, RyPES [Rydberg photoelectron spectroscopy?], and, for carbonyl complexes, infrared spectroscopy is useful. The overall results of such studies have shown that the relative $\sigma$-donor and $\pi$-acceptor capacities of the $SnCl_3$ ligand vary markedly as a function of the nature of the partners in the coordination sphere. Thus, in complexes of the type $PtCl(SnCl_3)L_2$ and $Pt(SnCl_3)_2L_2$ with $L = P(OR)_3$, the $SnCl_3$ *cis*-ligand diminishes competitively with the $\pi$-acceptor interaction $M \rightarrow P(OR)_3$. When $L = PR_3$, the influence of the $SnCl_3$ *cis*-ligand consists in a marked weakening of the $\sigma$-donor interaction $R_3P \rightarrow M$. In compounds of the type $[MCl_3CO(SnCl_3)_2]^{2-}$, where M = Rh(III) and Ir(III), the $SnCl_3$ ligands have the same influence on CO and the charge state of M as $PR_3$ in $MCl_3CO(PR_3)_2$, but in the complex $[MClCO(SnCl_3)_2]^{2-}$ the $SnCl_3$ ligand exhibits more pronounced $\sigma$-donor and $\pi$-acceptor properties than $PPh_3$ in $MClCO(PPh_3)_2$, such properties being more marked in the iridium(I) complex than in the rhodium(I) complex.

For this reason, in complexes of various types, the $SnCl_3$ ligand occupies different positions in the series based on the *trans*- or *cis*-influence and, depending on the nature of the other ligands, the influence itself is manifested unequally in the sense of the involvement in it of the $\sigma$-donor and $\pi$-acceptor interactions of M with $SnCl_3$. As a general characteristic of the mutual influence of ligands in such complexes, one may mention the tendency of $SnCl_3$ to have the minimum number of *trans*-partners L with $\sigma$-donor and $\pi$-acceptor properties [$L = PR_3$, $P(OR)_3$, CO, or $SnCl_3$]. *cis*-$SnCl_3$ exerts a dominant influence on the most pronounced properties of the ligand L ($\sigma$-donor or $\pi$-acceptor).

The influence of the central metal atom M on the state of the ligand $SnCl_3$ in a wide range of compounds cannot be investigated, since they differ significantly in composition and structure. For the complexes $[MX(SnX_3)_5]^{n-}$ and $[M(SnX_3)_5]^{m-}$ (X = Cl or Br), the 5*s*-electron-accepting capacities of $d^6$ and $d^8$ metals decrease in the sequences Ir(III) > Os(II) ≥ Ru(II) [32] and Pt(II) > Pd(II) > Rh(I) [33] respectively.

## 2. Heterogeneous Catalysts

As stated above (Section I), the main type of industrial heterogeneous catalytic systems comprises Pt–Sn alloys on various carriers. As mentioned above, apart from the alloys, the surface of the carriers contains also a whole series of tin(II) and tin(IV) compounds, each of which can play a definite role in complex catalytic processes. For example, in the case of catalysts consisting of a solid solution of $SnO_2$ in $MoO_3$ on the $SiO_2$ surface, the Mössbauer spectroscopic method demonstrated that the propene oxidation reaction leads to the formation of an adsorption complex of acroleine and tin(II),[91] which indicates unambiguously the involvement in the reaction of not only molybdenum(VI) compounds but also of tin(IV) and tin(II) compounds.

The results of the study of the Pt–Sn catalysts on various carriers[69–72,75,76] show that the composition of the compounds formed in a reductive medium on the surface is determined by

the composition of the deposited compounds and the properties of the carrier.

Mössbauer spectroscopic study of the phase composition of the Pt–Sn/$ZnAl_2O_4$ catalyst at all stages of its preparation as a function of the composition of the solution containing platinum and tin(II) compounds showed that, after deposition on the surface of the zinc–aluminium spinel, the main bulk of tin is present as $SnO_2$ and in a smaller proportion as the complex containing Pt–$SnCl_3$; when $SnCl_2$ is present in solution in an excess, tin(II) is formed on the surface with $\delta = 3.25$ and $\Delta = 1.85$ mm $s^{-1}$, indicating a strong interaction with the surface of the tin not bound to platinum.[69,71] In the course of the dehydrogenation of n-butane in a reductive medium, some of the tin(II) (both bound and not bound in the complex) forms alloys with platinum. The alloy composition depends on the Pt:Sn ratio in the complex predominating in the impregnating solution.[18,71] For Pt:Sn ratios of 1:1 and 1:2 in the complex, mainly the $Pt_3Sn$ alloy, which exhibits the highest catalytic activity among all Pt–Sn alloys and ensures a fairly high stability of the catalyst, is formed preferentially on $ZnAl_2O_4$.[18,71] The ratio $f'_{77}/f'_{293}$ for $SnO_2$ in such a catalyst is 7.7, which is appreciably higher than the corresponding parameter for massive $SnO_2$ and can indicate a high degree of dispersion of the particles on the carrier surface. The Mössbauer parameters of the alloys are close to those for the massive specimens, which was explained by the lower degree of dispersion of the particles of the Pt–Sn alloys compared with the state of $SnO_2$.[18]

Taking into account the values of $f'$ for the individual components of a similar catalyst, the kinetics of the formation of specific tin compounds on the surface have been investigated[75] by the Mössbauer method and a mechanism has been proposed for the oxidative dehydrogenation of paraffins. In the above study data were obtained for the first time demonstrating the strong interaction of part of the tin(II) with the carrier surface, leading to the formation of $SnAl_2O_4$.

When tin(II) and platinum(II) compounds with organic ligands were deposited on the $SiO_2$ surface with subsequent reduction, the formation of $SnSiO_3$ was observed by the Mössbauer method, which can also be regarded as a result of the insertion of tin(II) in the $SiO_2$ lattice with its subsequent partial reorganisation.[70] A detailed study has been made[76] of the genesis of the phase composition of the Pt–Sn catalyst on the $\eta$-$Al_2O_3$ carrier. A strong interaction of tin(II) with the surface was also observed and it was shown that the deposition of platinum(II) and tin(II) on the carrier in the form of an $SnCl_3$-containing platinum complex leads to their more intense interaction in the catalyst than in the case where the chlorides $PtCl_4^{2-}$ and $SnCl_4$ are deposited separately. It was found that the parameter $\delta$ for the alloys decreases linearly with increase of their platinum content and that the activity in dehydrocyclisation is associated with the modification of the properties of platinum atoms by tin.

The methodological problems arising in the analysis of the complex Mössbauer spectra of such catalysts were discussed above. In this connection the details of the identification of the types of compounds in the Pt–Sn catalyst deposited on $\gamma$-$Al_2O_3$, quoted by Bacaud and Bussiere,[77] must be treated critically. However, it is true that, as in catalysts incorporating other carriers, on the $\gamma$-$Al_2O_3$ surface there are several states of the tin(IV) and tin(II) atoms and several types of Pt–Sn alloys. This is also confirmed by the Mössbauer spectra of the Pt–Sn/$\gamma$-$Al_2O_3$ systems[18,73] resolved into the individual Lorentzian components by the second method (see above), which are illustrated in Fig. 5 (spectrum 5). Two states of tin(IV) [one close to $SnO_2$ and the other close to $SnCl_4$ and giving rise to a singlet (curve 5); both states interact with the carrier], two states of tin(II) [$SnAl_2O_4$ giving rise to a doublet (curve *1*) and $SnCl_2$ interacting with oxygen on the surface via Scheme (10) and giving rise to an $S_1$–$S_2$ doublet], and a series of Pt–Sn alloys ($Pt_3Sn$, singlet *4*; PtSn, singlet *3*; $PtSn_4$, singlet *2*) have been identified on the surface of this catalyst.[18]

Pt–Sn reforming catalysts, obtained by depositing $SnCl_3$-containing platinum complexes on $\gamma$-$Al_2O_3$ chlorinated beforehand [$\gamma$-$Al_2O_3$(Cl)] have been investigated by the Mössbauer method.[18,72,73] The Mössbauer spectra were analysed by Kuznetsov et al.[72] using the first resolution procedure and by Yurchenko[18] and Kuznetsov[73] using the second procedure (see above), according to which a preliminary study was made of the interaction of $SnCl_2$ with $\gamma$-$Al_2O_3$ and $\gamma$-$Al_2O_3$(Cl) during the preparation of the catalyst (Fig. 5, curves *1–4*). It was shown that prolonged treatment of the catalyst under conditions close to those during catalysis alters appreciably the quantitative composition of the tin-containing components (cf. spectra *6* and *7* in Fig. 5) and intensifies the interaction of part of tin(II) and $Al_2O_3$(Cl) with formation of tin(II) having $\delta$ close to that of anhydrous $SnCl_2$ (the singlet shown dashed in spectrum *7* in Fig. 5). More detailed characteristics of the state of tin(II) not bound to platinum on the surface were obtained by using for this purpose the temperature dependence of the parameter $f'$,[18,73] the extent of which can be deduced by comparing the Mössbauer spectra in Fig. 5 at 77 K (spectra *1–7*) and 293 K (spectra *1′–7′*). Otherwise, the two methods of analysis of the Mössbauer spectra yielded similar results not only as regards the identification of the principal tin containing components of the catalyst (cf. spectra 5 and *6* with Fig. 1 in Ref. 72) but also as regards their amounts on the surface.[18,73] It has been shown[18,72,73] that the modification of the carrier by introducing Cl atoms into the latter entails a significant change in the state of the tin(II) compounds in the catalyst.

The fundamental difference between the carriers based on $\gamma$-$Al_2O_3$ and $ZnAl_2O_4$ is that the former ensures a more ready susceptibility of tin(IV) to reduction and stabilises the state of tin(II) in tin-containing components of the catalyst.[18,72]

Thus the composition of the catalyst might have differed appreciably in different investigations as a consequence of the differences in the methods used to deposit platinum and tin, the conditions in the preliminary preparation of the $Al_2O_3$ surface, and, mainly, owing to the different nature of the carrier itself: $\gamma$-$Al_2O_3$,[10,72,73,76] $\eta$-$Al_2O_3$,[76] Zn–Al spinel,[69,71,75] and $SiO_2$;[70] they might also have differed owing to the differences between the procedures used in the analysis of the complex Mössbauer spectra of such systems discussed above.

Apart from the Pt–Sn alloys on carriers, which catalyse processes at high temperatures, the possibilities of the immobilised $SnCl_3$-containing complexes as heterogeneous catalysts of low-temperature processes have been attracting increasing attention recently. The first steps on these lines have already been taken. Thus it has been shown[85] that $[RhCl_4(SnCl_3)_2]^{3-}$ fixed on an anion-exchange resin catalyses the dimerisation of ethylene at 50–70 °C but the states of the complex on the anion exchanger and after exposure to the reaction conditions have not been investigated by the Mössbauer method. It has been shown[18] that carbonyltin halide complexes, which are active in the homogeneous-catalytic dehydrogenation of HCOOH (see Section III), can be immobilised on the $\gamma$-$Al_2O_3$ and $SiO_2$ carriers without loss of their catalytic properties. The Mössbauer parameters of the immobilised complexes indicate the interaction of a proportion of their $SnCl_3$ ligands via Scheme 10 with the surface OH groups; for example, such interaction of the complex [$PtCl_2$.

$.(SnCl_3)_2]^{2-}$ entails a change of $\delta$ from 1.64 to 1.52 mm $s^{-1}$ and of $\Delta$ from 2.11 to 2.2 mm $s^{-1}$; $f'$ increases and its temperature variation becomes less marked (Fig. 4). The Mössbauer parameters of the carbonyltin chloride complexes enumerated vary analogously.

## IV. CONCLUSION

Extensive information has thus been accumulated about the Mössbauer effect involving the $^{119}Sn$(II, O) nuclei in various tin halide complexes, clusters, and intermetallic compounds. Tin(IV) compounds, including organotin compounds, have been studied even more vigorously.[11] All these data have created a basis for a wider-scale employment of the Mössbauer method in the study of the structure and properties of various homogeneous and heterogeneous tin-containing catalysts.

The lack of exact values of $f'$ and of their temperature variation for many individual compounds and (especially) for the products of the interaction with the carrier constitutes a major problem, which has inhibited extensive quantitative studies of tin-containing catalysts by the Mössbauer method. It would be useful to obtain general quantitative relations between $f'$ and the parameters characterising the degree of interaction of tin-containing molecules with the carrier surfaces, particularly the relations for the corresponding equilibrium constants and force constants of the adsorbent–adsorbate bonds, using additional information from their vibrational spectra. Studies of the temperature dependence of $f'$ at lower temperatures, down to the temperature of liquid helium, are essential. In general, whereas the parameters $\delta$, $\Delta$, and $\Gamma$ have been used fairly widely in the study of the state of tin-containing catalytic systems, the parameter $f'$ has not as yet become a widely used means for the investigation of the properties of real catalysts. However, modern technology and the need to develop precise methods for the investigation of the state of heterogeneous M–Sn catalysts will probably correct this situation in the immediate future.

Finally, the greatest problem in heterogeneous catalysis is that of the development of methods for the investigation of the properties of the surfaces of real catalysts. The Mössbauer effect could, in principle, become a basis for such a method. However, a recent international conference on the application of the Mössbauer effect (Alma-Ata, 1983) demonstrated that so far the different versions of the method make it possible to investigate a surface layer which is not less than tens and even hundreds of angstroms thick, whereas for catalysis one requires information about the state of the Mössbauer atoms and the depth equivalent to several monolayers, i.e. up to 10 Å. Presumably Mössbauer spectroscopy, which is already a unique method for the investigation of the state and properties of homogeneous and heterogeneous catalysts containing Mössbauer atoms, will in future occupy a leading position in the study of such systems.

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# The Nature of the Active Component in Deposited Sulphide Catalysts

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The use of various physical methods (high resolution electron microscopy, Mössbauer spectroscopy, X-ray photoelectron spectroscopy, X-ray radial distribution of atoms, infrared spectroscopy, and the study of the long-range fine structure of X-ray absorption) for the elucidation of the structure of the active component in deposited sulphur catalysts is examined. The data obtained by these methods show that the active component in the catalysts considered has an $MoS_2$ (or $WS_2$) layer structure, while cobalt (or nickel) ions are distributed on the lateral faces of the dispersed sulphide particles.
The bibliography includes 63 references.

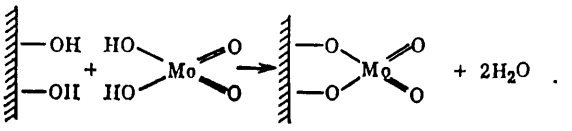
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## I. INTRODUCTION

The catalysts used in practice usually consist of a complex mixture of bulk-phase and surface compounds. As a rule the catalytically active centres are incorporated in highly dispersed phases. The composition of the catalyst varies under the influence of the reaction medium. All these factors are responsible for the difficulties which arise in the solution of the problem of which of the compounds (or their combination) is essential for the manifestation of catalytic activity (i.e. is an active component of the catalyst). For the majority of the important industrial catalysts, this problem is still controversial. The most likely controversy in recent years arose in the discussion of the mechanism of the action of hydro-purification catalysts. Industrial catalysts for the refining of petroleum products by treating them with hydrogen at high temperatures contain molybdenum (or tungsten) compounds combined with cobalt (or nickel) compounds in a highly dispersed state on a carrier (alumina). Under the conditions of the reaction medium, the catalysts combine with sulphur (the formation of surface metal sulphides). In the course of hydro-purification at high temperature (350–450 °C) under a high hydrogen pressure (50–100 atm), C–S, C–N, and C–O bonds undergo hydrogenolysis (which leads to the removal of hetero-atoms from the petroleum products—in the first place the removal of sulphur in the form of hydrogen sulphide), metallic impurities are removed from the petroleum crude, and hydrogenation and isomerisation processes take place. Hydro-purification is one of the largest-scale catalytic processes (hundreds of millions of tonnes of petroleum products are processed). The annual production of hydro-purification catalysts runs into tens of thousands of tonnes. The scale of the employment of hydro-purification processes and of the manufacture of catalysts for this purpose will increase with increasing extent of the processing of petroleums having a high sulphur content (and, in future also, of the liquid products of the processing of coal). For example, in the USA these catalysts occupy the first place as regards the rate of growth of production and sales.[1–3] Industrial hydro-purification catalysts contain 12–20% of transition metal oxides on a carrier. The cost of the metals forming part of the composition of these catalysts is rapidly increasing. For example, the world prices of cobalt rose by a factor of 4 during the period from 1970 to 1976.[4] This makes it necessary to create active and stable catalysts with a low metal content. For the solution of this problem, it is important to understand the nature of the active component in the catalyst. Nevertheless, there is no unanimous view in the literature concerning the nature of such a component in sulphide catalysts. The most important of the proposed hypotheses are illustrated in Figs. 1–4.

The monolayer model (Fig. 1) has been put forward by Lipsch and Schuit[5] to account for the structure of the active component in hydrosulphurisation catalysts and improved models of this type have been considered in other studies.[6,7] This model is based on the hypothesis that surface oxide sulphides are formed in the monolayer of the surface aluminium molybdate when the latter combines with sulphur. The molybdate is produced in accordance with the mechanism




Cobalt is located within the $Al_2O_3$ lattice, but its role in the catalytic process remains obscure.

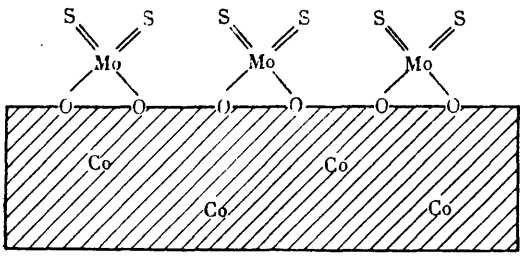



**Figure 1.** The monolayer model designed to account for the structure of the active component in hydrodesulphurisation catalysts.[5–7]

The intercalation model (Fig. 2) has been proposed by Voorhoeve and Stuiver[8] and improved by Farragher and Cossee.[9] According to this model, different metal ions can be inserted (intercalated) between sulphide packets linked by weak van der Waals forces. Farragher and Cossee[9] believe that intercalation of the Ni(Co) ions between

$MoS_2(WS_2)$ layers is confined to the surface of the lateral face. Thus the active centre is produced on the lateral face of the sulphide crystal; there is also a possibility of the formation of bimetallic active centres, including those incorporating $Mo^{3+}$ and $W^{3+}$ ions after the partial elimination of sulphur from the surface layer. Fig. 2 illustrates schematically the structure of the $MoS_2$ layer crystals; a similar scheme is valid for $WS_2$. The crystals of these sulphides consist of packets having the composition $MS_2$ and each packet comprises a layer of metal (M) atoms and two layers of sulphur atoms. A metal atom within the layer is coordinated to six sulphur atoms.

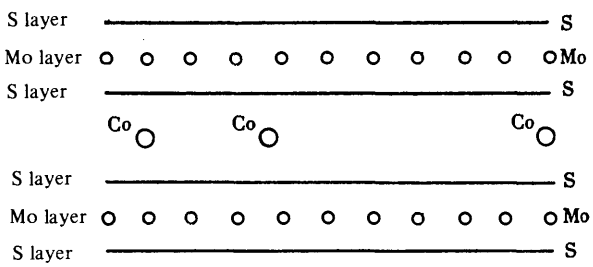



**Figure 2.** The intercalation model.[8,9]

The contact synergism model, proposed by Delmon and co-workers,[10-12] presupposed (Fig. 3) that two separate (albeit very disperse) sulphide phases are formed in mixed sulphide catalysts. These phases are in contact or are close to one another on the carrier. The active centres proper are distributed on the $MoS_2$ phase. The presence of cobalt sulphide activates the hydrogen.

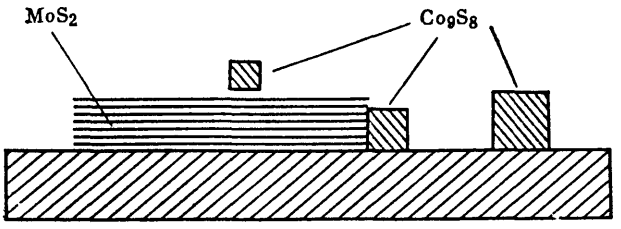



**Figure 3.** Delmon's "contact synergism" model.[10-12]

The insertion model has been put forward recently by Ratnasamy and Sivasanker.[13] In this model it is assumed that the cobalt atom is located on the lateral face of the $MoS_2$ crystal. Fig. 4 illustrates the lateral face of a single $MoS_2$ packet with inserted cobalt atoms. This model was put forward[13] without experimental justification on the hypothesis that the location of cobalt on the lateral face decreased the excess charge on the sulphur atoms adjoining the lateral face.

The application of a combination of physical methods has led in recent years to significant progress in the elucidation of the composition of the active component of hydropurification catalysts. The aim of the present review is not a complete retrospective consideration of all the data obtained in the study of hydrodesulphurisation catalysts (frequently extremely contradictory), since many excellent reviews covering this field already exist (see, for example, Refs. 13–17). Here we shall deal with the results of recent studies of two catalytic systems: $(Ni+W)/SiO_2$ (studies performed at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences[18-36]) and $(Co+Mo)/Al_2O_3$ (studies carried out by Topsøe and co-workers[14,37-54]).

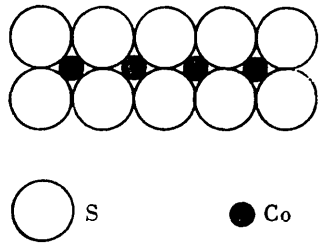



**Figure 4.** The insertion model.[13]

## II. RESULTS OF THE STUDY OF THE $(Ni+W)/SiO_2$ SYSTEM

### 1. Characteristic Features of the Preparation of the Catalysts

Silica gel was used as the carrier for the preparation of the catalytic system, because it ensures a more uniform surface composition (compared with catalysts based on $Al_2O_3$) and a lesser degree of interaction of the deposited components with the carrier.

In order to attain the maximum degree of dispersion of the sulphide particles, the surface sulphides were obtained from attached organometallic complexes. The preparation of the catalyst is illustrated schematically in Fig. 5.

The preparation of catalysts incorporating only one metal (such catalysts are referred to below as monometallic) involved states in which the allyl complexes of tungsten and nickel interacted with the surface hydroxy-groups, the resulting attached complexes were treated with hydrogen, and the reduced forms of nickel (finely dispersed metallic nickel) and tungsten ($W^{2+}$ ions) were subsequently converted into sulphides. The catalysts obtained in this way (henceforth such catalysts will be referred to as organometallic) were 5–20 times more active than the catalysts prepared by the standard method involving impregnation with $Ni(NO_3)_2$ and $(NH_4)_2WO_4$ solutions.[18,31] This difference in activity is associated mainly with the higher degree of dispersion of the sulphide particles and catalysts prepared from organometallic complexes (organometallic catalysts).

The monometallic sulphide catalysts $Ni/SiO_2$ and $W/SiO_2$ (the sulphur incorporated in the catalysts when it combines with them will not be indicated in the formulation of the catalyst composition either here or henceforth) exhibited approximately equal activities in the hydrogenolysis of thiophen at 300–350 °C. Analogous data indicating similar activities of cobalt and molybdenum sulphide deposited on charcoal have been published by De Beer et al.[55] Thus it

would not be useful to regard the sharp increase in the activity of the mixed sulphide systems (such systems are referred to below as "bimetallic") as "promotion" (this term is suitable for the case where one of the components is inactive or its activity is low). The mutual enhancement of activity in mixed sulphide systems is usually treated in the literature as a manifestation of synergism.

The most active bimetallic catalysts on $SiO_2$ have been obtained when the second component was deposited in the form of an organometallic compound on the dispersed sulphide of the first component (see Fig. 5). It is important to note that the $(Ni+W)/SiO_2$ sulphide catalysts of "organometallic" origin were more active than catalysts of analogous composition on alumina.[31]

The activity of the catalysts depends on the atomic ratio of the deposited metals (Fig. 6). The dependence of the overall activity $a$ on $\lambda = Ni/(Ni+W)$ is analogous for organometallic hydrodesulphurisation catalysts and the specimens obtained by the usual procedures.[10,42,56]

The maximum activity per unit weight of the deposited metals in the "organometallic" catalysts is observed at $\lambda \cong 0.3$; the activity referred to 1 g of nickel increases with decrease of its content and reaches a maximum at $\lambda \leq 0.2$. Presumably for these values of $\lambda$ the entire nickel (or at least a constant fraction of the latter) is incorporated in the composition of the active centres. We may note that analogous results have been obtained for the $(Ni+Mo)/SiO_2$ system.[24]

## 2. High Resolution Electron Microscope Data

The morphology of the sulphide particles in the $(Ni+W)/SiO_2$ catalysts has been investigated[22,24,32] with the aid of a JEM-100CX electron microscope with a point resolution of 2 Å (Figs. 7 and 8). The photomicrographs of the monometallic $Ni/SiO_2$ and $W/SiO_2$ sulphide catalysts obtained from organometallic complexes show, against the background of $SiO_2$ globules, individual particles with dimensions <10 Å.

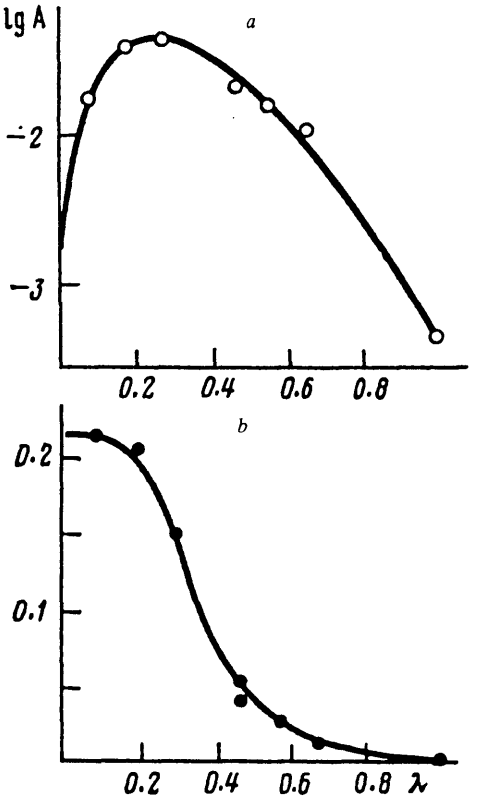



**Figure 6.** Dependence of the catalytic activity of the $(Ni+W)/SiO_2$ sulphide catalysts on the atomic ratio $\lambda = Ni/(Ni+W)$; the activity was measured in the hydrogenolysis of thiophen at 350 °C and 20 atm: *a*) activity (rate of reaction) referred to 1 gram-atom of both metals (Ni + W) ($10^2$ mol $s^{-1}$); *b*) activity referred to 1 gram-atom of nickel ($10^2$ mol $s^{-1}$).

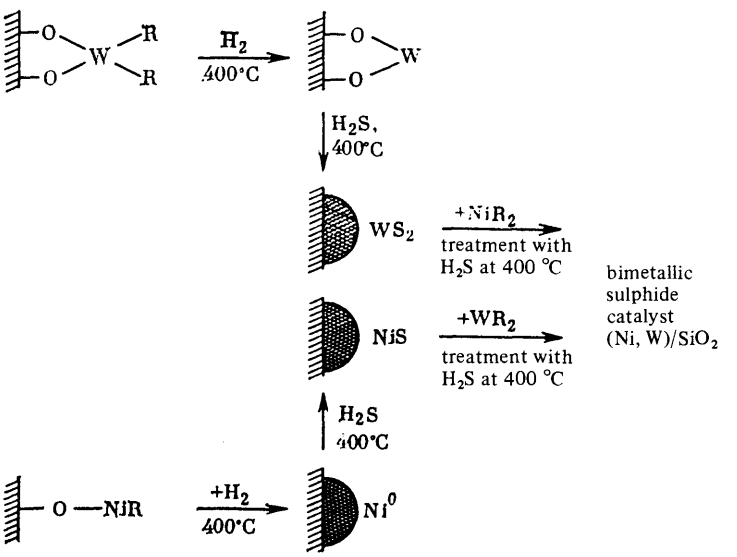



**Figure 5.** Schematic illustration of the preparation of deposited mono- and bimetallic catalysts using organometallic complexes.

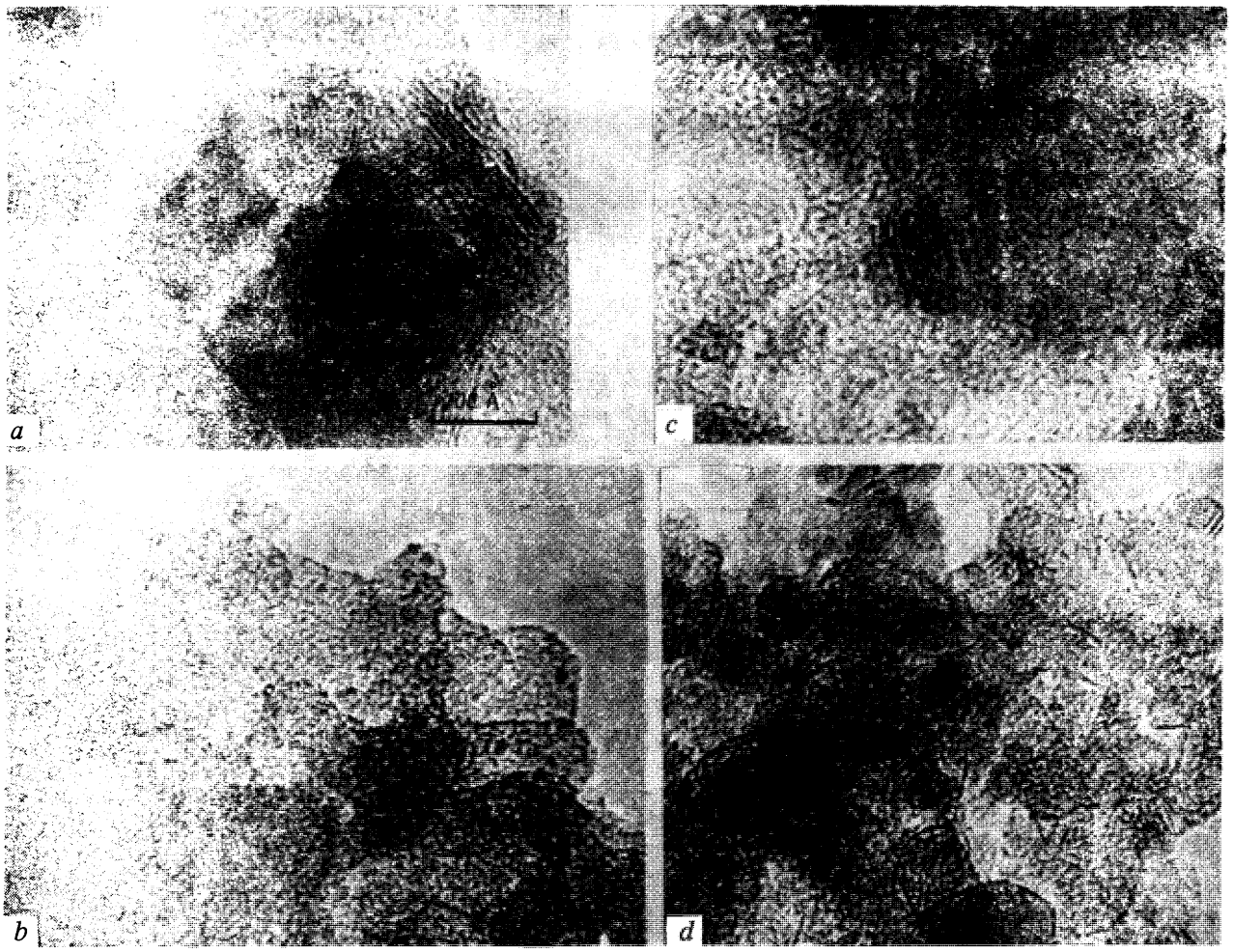



**Figure 7.** Electron photomicrographs of deposited sulphide catalysts: *a*) $WS_2/SiO_2$ catalyst obtained by the standard impregnation method; *b*) $W/SiO_2$ catalysts obtained from organometallic compounds fixed to the carrier; *c*) $(Ni+W)/SiO_2$ catalysts obtained by the standard method involving simultaneous impregnation with aqueous $Ni(NO_3)_2$ and $(NH_4)_2WO_4$ solutions; *d*) $(Ni+W)/SiO_2$ catalyst obtained by treating a $W/SiO_2$ specimen with the allyl complex of nickel and subsequent sulphiding at 400 °C.

In the case of catalysts obtained by "standard" impregnation methods, particles of nickel and tungsten sulphides can be seen. Thus the photomicrographs of the catalyst containing $WS_2$ show formations whose size ranges from 20 to several hundred angstroms. These agglomerates have a layer structure with interlayer distances of ~6 Å, which corresponds to a distance $d_{002} = 6.2$ Å between individual layers of tungsten atoms in the $WS_2$ crystal. Comparison of the dimensions of the sulphide particles in the "standard" and "organometallic" catalysts shows that the higher activity of the latter can be accounted for in the main by the higher degree of dispersion.[22,32]

A different morphology of the surface particles is characteristic of the bimetallic sulphide catalysts compared with that of the monometallic $W/SiO_2$ specimens of "organometallic" origin. Instead of particles approximately 10 Å in size, linear structures (strips) 20–50 Å long appear in the sulphur-treated $(Ni+W)/SiO_2$ catalyst. The photomicrographs of the "organometallic" specimens show mainly single strips; when packets of strips are formed, the distance between the strips "layers" is about 6 Å. Evidently the individual strips are projections of the $WS_2$ layers onto the lateral surface.

The numbers of layers in the surface particles of the "organometallic" and "standard" catalysts differ significantly (Fig. 8). The dominant type of particles in the most dispersed organometallic catalyst consist of single-layer formations. In the "standard" catalysts the sulphide particles contain 6–10 layers.[32] Comparison of the activities of the "organometallic" and "standard" catalysts with the morphology of the sulphide particles in them provides evidence in support of the view that the active centres are located on the lateral faces of the sulphide particles (Fig. 9). The activity of the "organometallic" catalysts is ~3 times higher than that of the "standard" catalysts. We shall assume that the active centres are located on the basal plane. In this case a greater difference should be observed between the activities, since, on passing from the "organometalic" to "standard" specimens, the fraction of the surface of the basal planes per unit mass of the active phase (and

hence the catalytic activity) should fall approximately in proportion to the increase of the number of layers in the particles of the surface sulphide.

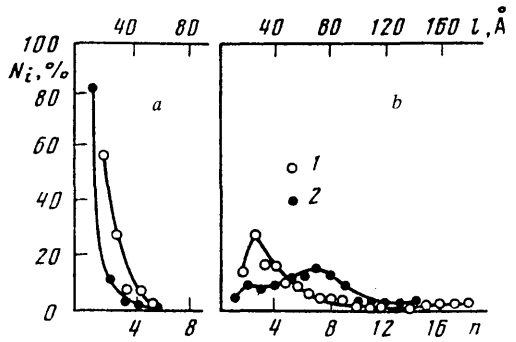



**Figure 8.** Distribution of particles with respect to size in the $(Ni+W)/SiO_2$ sulphide catalysts according to electron microscope data: *a*) catalyst obtained from organometallic compound; *b*) catalyst obtained by the standard impregnation method; *1*) length of layers *l*; *2*) number of layers *n*; $N_i$ = fraction of particles (%).

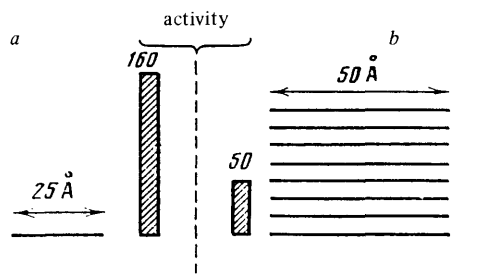


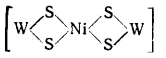

**Figure 9.** Comparison of the typical surface structures in the deposited sulphide catalysts $(Ni+W)/SiO_2$ according to electron microscope data; the lines correspond to individual $WS_2$ layers; the catalytic activity is expressed as the rate of hydrogenolysis of thiophen at 350 °C [$10^{-4}$ mol (Ni + W g-atom)$^{-1}$ $s^{-1}$]: *a*) catalyst obtained from organometallic compounds; *b*) catalyst obtained by the standard impregnation method.

It follows from the results that (a) layer structures characteristic of massive $WS_2$ or $MoS_2$ sulphides are formed in the bimetallic sulphide catalysts. The most dispersed "organometallic" catalysts with an enhanced activity contain single-layer formations (single packets). This finding is inconsistent with the intercalation model[8,9] which presupposes not less than two layers of packets for the formation of active centres. (b) The most probable site at which the active centres for the hydrogenolysis of the C–S bond are located on the lateral faces of $WS_2$ or $MoS_2$ crystals.

The results of electron microscope studies do not, however, permit an unambiguous conclusion about the formation of mixed compounds from nickel and tungsten sulphides.

### 3. X-Ray Photoelectron Spectroscopic (XPES) Data

When dispersed nickel or tungsten (molybdenum) sulphides are formed on the surface of silica gel, an appreciable increase of the electron binding energy $E_b$ at the $Ni2p_{3/2}$ and $W4f_{7/2}$ levels is observed in the XPE spectra (Fig. 10) compared with the massive sulphides.[19,33] This indicates the interaction of the dispersed sulphides with the carrier with a consequent decrease of the electron density on the deposited metals. When mixed catalysts are prepared, a further increase of $E_b$ at the $Ni2p_{3/2}$ levels and a decrease of $E_b$ at the $W4f_{7/2}$ and $(Mo3d_{5/2})$ levels takes place. Thus the introduction of nickel into the composition of dispersed sulphide catalysts leads to its interaction with tungsten (molybdenum), which entails the transfer of electron density from nickel to W(Mo) atoms. We may note that the absolute values of $E_b$ at the $Ni2p_{3/2}$ and $W4f_{7/2}$ levels for the catalysts and the thiotungstate and thiomolybdate complexes containing the $[Ni(MS_4)_2]^{2-}$ anion, where M = Mo or W, are similar. In these compounds nickel is surrounded by sulphur atoms:



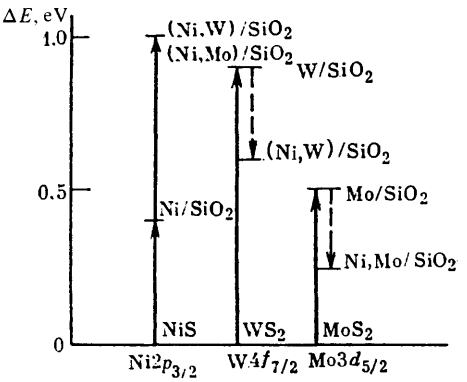



**Figure 10.** The change in the energies of the $Ni2p_{3/2}$, $W4f_{7/2}$, and $Mo3d_{5/2}$ electronic levels in deposited mono- and bi-metallic sulphide catalysts relative to the NiS, $WS_2$, and $MoS_2$ massive sulphides.

Thus the application of the XPES method established that mixed sulphide compounds are indeed formed in the bimetallic catalysts. In order to elucidate the structure of the mixed compounds produced, it is necessary to resort to structural data.

### 4. Data Obtained by Structural Methods

Deposited sulphide catalysts obtained from attached organometallic compounds are amorphous to X-rays. Information about the interatomic distances in the highly dispersed particles of the deposited catalysts can be obtained by the X-ray atomic radial distribution (XARD) method.[57,58] The XARD curves for deposited sulphide catalysts are presented in Fig. 11. The following interatomic distances, which are satisfactorily correlated with the values characteristic of $WS_2$, have been determined for the $(Ni+W)/SiO_2$

sulphide catalysts:[34] ~2.5 Å (W–S distances in the $WS_2$ layer amounting to 2.48 Å; ~3.2 Å (W–W distance amounting to 3.187 Å); ~4.1 Å (distance between the W atoms and the S atoms in the second coordination sphere amounting to ~4.04 Å). At the same time the XARD curves for the deposited catalysts show a peak at ~3.8 Å, which was not observed in the study of the $WS_2$ structure.

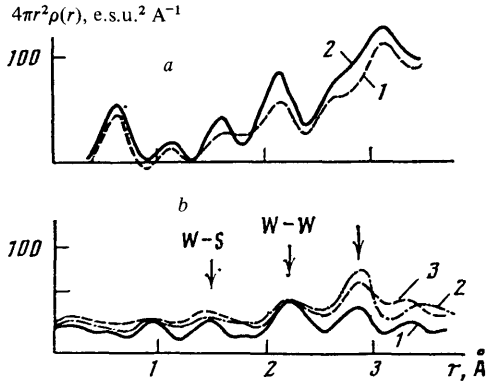



**Figure 11.** *a*) radial distribution curves for the carrier ($SiO_2$) (curve *1*) and the sulphur-treated $W/SiO_2$ catalyst prepared from organometallic precursors (curve *2*); *b*) differential radial distribution curves for the sulphur-treated catalysts obtained after subtracting the curve corresponding to the carrier: *1*) $W/SiO_2$ specimen obtained from organometallic precursors; *2*) $(Ni+W)/SiO_2$ specimen obtained from organometallic precursors; *3*) $(Ni+W)/SiO_2$ specimen obtained by the standard impregnation method.

The same interatomic distances have been found for the bimetallic sulphide catalysts as for the monometallic catalysts. Thus the surface compounds in the deposited $W/SiO_2$ and $(Ni+W)/SiO_2$ sulphide catalysts have the structure of massive $WS_2$. An analogous conclusion is valid for the deposited molybdenum catalysts.

The introduction of nickel does not entail the appearance of new peaks on the X-ray plots (or XARD curves) for the deposited sulphide; only the intensities of certain maxima, characteristic of the $W/Si_2$ catalysts, increases. The increase of the intensity of the maxima can also be associated with the formation of $WS_2$ layers ~25 Å long (instead of the more dispersed formations).

If nickel ions are intercalated between $WS_2$ layers, one might have expected the appearance of the maximum corresponding to an Ni–W distance of 3.45 Å. Since this peak was not observed, one may conclude that intercalation compounds are not formed in the mixed sulphide catalysts; the Ni–Ni distance characteristic of nickel sulphides (3.4 Å) is also absent.

It is noteworthy that the peaks corresponding to the W–W distances between the atoms in different packets of the $WS_2$ structure are not manifested on the XARD curves for the deposited sulphide catalysts. These results are consistent with electron microscope data, according to which single $WS_2$ packets are formed preferentially on the surface and, when aggregates are produced, the layers in the latter are not arranged in parallel.

The appearance of a maximum of 3.8 Å, which does not correspond to the interatomic distances in the $WS_2$ structure, has been explained[34] by the appearance of a chemical bond between the deposited sulphides and the carrier with formation of Si–O–W–S fragments. In these fragments the Si...W distance is ~3.8 Å. Comparison of the $WS_2$ structure with that of the $SiO_2$ surface layers shows that the W–W and S–S interatomic distances in $WS_2$ are close to the O–O interatomic distances in two neighbouring $SiO_4$ tetrahedra forming the $SiO_2$ structure. The surface layer sulphide compounds of tungsten can therefore be formed without distorting the structure of the layer.

Thus it follows from the XARD data that (a) the $WS_2$ layer structure is retained in the deposited sulphide catalysts without the formation of a regular three-dimensional structure; (b) the appearance of the maximum corresponding to an interatomic distance of 3.8 Å, which is not observed in $WS_2$ and $SiO_2$, may be due to the formation of chemical bonds between the deposited sulphides and silica gel.

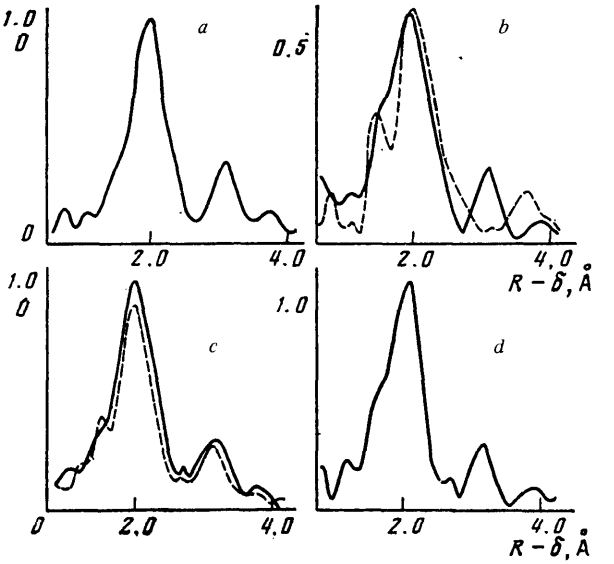



**Figure 12.** Radial distribution curves obtained by the EXAFS method in the measurement of the $L_{III}$ spectrum of tungsten in the sulphided catalysts: *a*) massive $WS_2$ sulphide; *b*) $W/SiO_2$; *c*) $(Ni+W)/SiO_2$, $\lambda = 0.3$; *d*) $(Ni+W)/SiO_2$, $\lambda = 0.5$; the dashed lines correspond to specimens brought into contact with air; $U$ = relative intensity (arbitrary units); $R$ = interatomic distance; $\delta$ = phase shift.

Additional data for the structure of the surface sulphide compounds have been obtained by the EXAFS method (the principles of the method in relation to the study of catalysts have been described by Mastikhin and Zamaraev[59]).

In order to determine the interatomic distances characteristic of the environment of the tungsten atom, the $L_{III}$ absorption spectra of this element have been recorded.[35] The radial distribution curves are illustrated in Fig. 12. Peaks corresponding to the W–S (~2.46 Å) and W–W (~3.19 Å) interatomic distances characteristic of the $WS_2$ packet were found for the $W/SiO_2$ catalyst. A maximum at $R-\delta = 1.61$ Å was also observed, which may be due to the presence of oxygen in the coordination spheres of the tungsten ions (Si–O–W fragments linking the ultradispersed particles of tungsten sulphide to the carrier

surface). The introduction of nickel into the composition of the catalyst increases the intensity of the peaks at $R-\delta = 2.05$ and 3.09 Å. It has been suggested[35] that this may be caused by the additional scattering by nickel ions. When account is taken of the phase correction for the scattering by nickel ions, the W–Ni distances should be 2.38 and 3.42 Å in this case. Analysis of the *K* absorption spectra of the nickel in the mixed sulphide catalyst showed that there are sulphur ions in the immediate environment of nickel. The Ni–S distance is 2.22 Å, which is significantly less than the Ni–S distance in α-NiS (2.38 Å). These data confirm the conclusion that the Ni–S phase is absent from the bimetallic catalysts. The Ni–S distance of 2.22 Å is close to that characteristic of the Ni–S bond length in $[Ni(WS_4)_2]^{2-}$, where the nickel is present in a planar square made up of sulphur ions.

### 5. The Structure of the Active Component of the $(Ni+W)/SiO_2$ Sulphide Catalyst

By the active component, we understand surface structures containing the active centres for the catalytic reaction. The active centre should be understood as the minimum number of surface atoms necessary for the occurrence of the catalytic cycle.

When models of the active component and of the active centre in deposited sulphide hydrosulphurisation catalysts are considered, account must be taken of the following experimental facts observed in the course of the investigation of the $(Ni+W)/SiO_2$ system prepared from organometallic compounds: (a) highly dispersed sulphide particles are present on the catalyst surface mainly in the form of monolayer structures comprising individual packets with linear dimensions of ~25 Å; (b) mixed compounds of two metals (nickel and tungsten in the case considered) are formed on the surface; (c) the interatomic W–S (2.46 Å) and W–W (3.20 Å) distances in the highly dispersed sulphide particles correspond to the layer structure of the massive tungsten sulphide; (d) maxima, which can be referred to the W–O (1.93 Å) and Si–W (3.8 Å in the Si–O–W fragment) distances, are observed on the radial distribution curve; (e) sulphur ions are present in the first coordination sphere of nickel at a distance of ~2.22 Å. Nickel ions are apparently distributed at distances of 2.32 and 3.42 Å from the tungsten ions.

It follows from the data obtained that the active component has the layer structure typical for $WS_2$ (or $MoS_2$) crystals. The active component may be a single packet comprising two layers of sulphur atoms and a layer of W (or Mo) atoms between them. This packet can be arranged either parallel to the carrier surface [can adjoin the carrier via its basal plane (Fig. 13*a*)] or at right angles to the surface, i.e. can adjoin the carrier via its lateral face (Fig. 13*b*). According to electron microscope data, the second possibility is more likely. A cross section for such a packet is illustrated in Fig. 14. Some of the tungsten atoms are linked to the oxygen atoms on the carrier surface. The appearance of the more negative (compared with sulphur) oxygen in the coordination sphere of the tunsten ion leads to a difference between the positions of the electronic levels of tungsten in the dispersed surface particles compared with massive $WS_2$. The nickel atoms are located on the lateral face of the active component, being distributed in the same plane as the tungsten atoms. Fig. 14 illustrates two possibilities for the adsorption of a thiophen molecule: on a bimetallic active centre (Fig. 14*a*), after the removal of a single sulphur atom from the surface of the active component, and on a monometallic active centre (Fig. 14*b*).

The structure presented in Fig. 13*b* contains Si–O–W fragments with an Si–W distance of ~3.8 Å, which corresponds to the peak on the XARD curve.

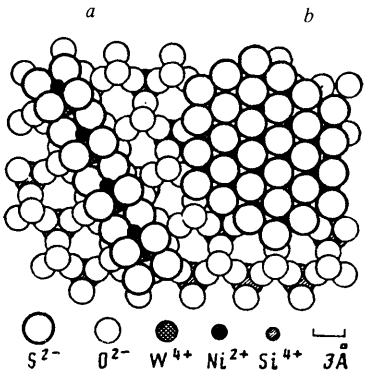



**Figure 13.** Distribution of the $WS_2$ packets on the silica gel surface: *a*) packet arranged at right angles to the $SiO_2$ surface, adjoining it via its lateral face; *b*) packet in contact with the $SiO_2$ surface via its basal plane.

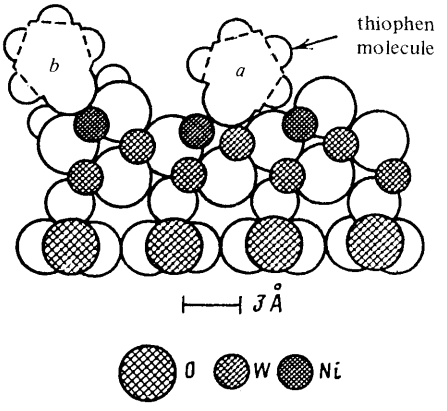


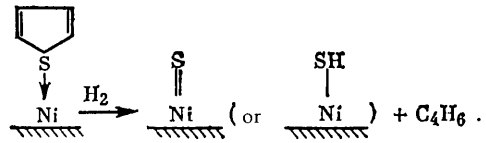

**Figure 14.** The possible structure of the active component in the sulphide hydrodesulphurisation catalysts.

In the study of the structures of the active centres on sulphide catalysts, it is important to determine the location of the nickel (or cobalt) ions in the layer structure of the active component. The possible structures formed when the nickel atoms are distributed on the lateral face of the $WS_2$ crystal have been examined in detail.[36] The best correspondence with structural data has been observed on the hypothesis that the nickel atom substituting a tungsten atom is surrounded by sulphur atoms on the lateral face (Fig. 14). Findings such as the appearance of shortened Ni–S distances and two types of interatomic Ni–W distances can then be explained.

We shall examine the possible types of active centre.

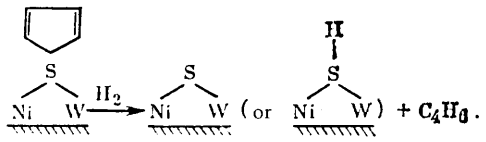
(a) A monometallic active centre—a coordination-unsaturated nickel ion. After the adsorption of thiophen and its hydrogenolysis on such a centre, the sulphur atom is bound

to one metal ion:



The role of tungsten sulphide then reduces to providing the lateral faces of its crystal as a matrix for the accommodation of the coordination-unsaturated nickel ions.

(b) A bimetallic active centre. In this case $WS_2$ plays the role not only of the matrix for the stabilisation of the nickel ions but also participates directly in catalysis. In the course of the hydrogenolysis of thiophen, a sulphur atom is bound to two metal ions:



It has been shown[36] that the removal of surface sulphur, bound to two metal atoms, require a significantly greater energy expenditure than the removal of the sulphur bound to one nickel (or cobalt) atom. The successive removal and addition of sulphur to the monometallic active centre in the catalytic cycle is therefore more likely. The existence of the optimum ratio $\lambda = Ni/(Ni+W) = 0.3$ can be explained with the aid of the above model of the binding of nickel ions on the tungsten sulphide surface. The above value is close to the atomic fraction of the nickel stabilisation centres on the lateral faces of tungsten sulphide packets with a size of 20–50 Å. When the nickel content is above the optimum value, the activity falls (for example, down to 10% of the maximum activity for $\lambda = 0.6$), apparently as a consequence of the shielding of the active centres by nickel sulphide.

The model of the active component considered above has certain features of the "monolayer model" (retention of the bond between the sulphide species and the carrier), the Cossee model (distribution of the ions of the second metal on the lateral face of the sulphide), and the Ratnasamy "insertion" model (distribution of nickel on the lateral plane of a single sulphide packet; square coordination of the nickel ion), but is inconsistent with Delmon's synergistic model (Fig. 3). The results of the study of the $(Ni+W)/SiO_2$ system confirmed the principal postulates of the hypothesis put forward by Topsøe concerning the nature of the active component on cobalt plus molybdenum sulphide/alumina desulphurisation catalysts.

## III. RESULTS OF THE STUDY OF THE $(Co+Mo)/Al_2O_3$ SYSTEM

The $(Co+Mo)/Al_2O_3$ system is used widely as an industrial hydropurification catalyst (nickel is sometimes used instead of cobalt). The catalysts are usually prepared by the successive impregnation of the carrier with aqueous solutions of the components followed by heat treatment in air at 500 °C and conversion into the sulphide form. A number of studies have been made on this system (see the relevant reviews[14–17,53]), but these did not yield unambiguous data owing to the inhomogeneity of the surface composition of the given system (particularly in the oxidised state) and the high degree of dispersion of the active component. As a result of the systematic studies by Topsøe and co-workers[14,37–54] by various physical methods, more reliable information about the nature of the active component in this system has been obtained only in recent years.

### 1. Mössbauer Emission Spectroscopic Data

Systematic application of this method to the study of sulphide systems yielded important information about the nature of the active component in the system considered. It has been noted[14,39] that this is associated with the following features of the method: (a) the Mössbauer parameters (the isomer shift $\delta$, the quadrupole splitting $\Delta E_Q$) are very sensitive to the oxidation state and the composition of the immediate environment of the element investigated; (b) Mössbauer spectra can be measured directly under reaction conditions (at an elevated temperature and in the reaction medium with the necessary composition).

The principal data have been obtained using Mössbauer emission spectroscopy (MES). In the study of sulphide catalysts, mainly specimens into which $^{57}Co$ had been introduced were used. The details of the method have been described in detail elsewhere.[38,39,60] The advantage of the MES method compared with another method [X-ray photoelectron spectroscopy (XPES)] which makes it possible to obtain information about the electronic state of a given element, are evident from a comparison of the spectra (Fig. 15). Whereas the XPE spectra of metallic cobalt and its compounds are virtually identical, the ME spectra differ sharply.

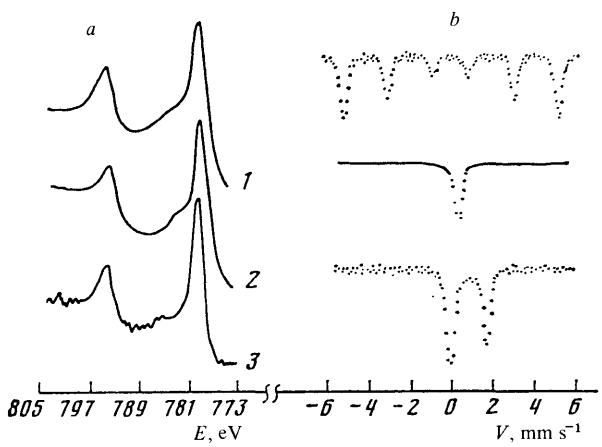



**Figure 15.** X-Ray photoelectron Co2*p* spectra (*a*) and Mössbauer absorption spectra of the individual compounds (b); $E$ = bond energy (eV); $V$ = velocity; *1*) metallic cobalt; *2*) $Co_9S_8$; *3*) $CoMo_2S_4$.[14]

In the first studies[37,38] involving the application of MES, the authors already concluded that in the cobalt–molybdenum sulphide catalysts cobalt is present in a compound different from $Co_9S_8$ and $CoMo_2S_4$; the compound has been called the "Co–Mo–S phase". The ME spectrum of this phase is characterised by a doublet $Q_1$ (Fig. 16), whose parameters differ from those of the individual compounds. The spectra of the sulphide catalysts show, together with the doublet $Q_1$, a weak signal (a doublet $Q_2$) corresponding to the same state of cobalt in which it existed before being converted

into the sulphide (apparently these are cobalt ions bound to the carrier).

A detailed study of the formation of the "Co–Mo–S phase" as a function of the composition and conditions in the preparation of the catalysts[40–48] permitted the following principal conclusions:[47,53]: (a) the "Co–Mo–S phase" is not a stoichiometric compound of definite composition; (b) the cobalt atoms in the "Co–Mo–S phase" are surrounded by sulphur atoms; (c) the "Co–Mo–S phase" is present in both deposited catalysts, obtained using various carriers ($Al_2O_3$, $SiO_2$, activated charcoal), and in massive mixed catalysts; (d) the cobalt atoms are present on the surface, since their environment changes after the adsorption of oxygen; (e) there is a correlation between the content of the "Co–Mo–S phase" in both deposited and massive catalysts and the catalytic activity in hydrodesulphurisation.

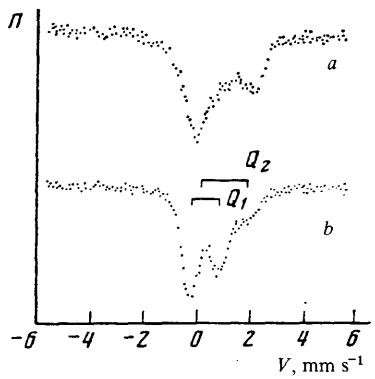



**Figure 16.** Mössbauer emission spectra of the $(Co+Mo)/Al_2O_3$ catalysts:[42] *a*) catalyst in the oxidised state; *b*) after treatment with the $H_2S+H_2$ mixtures; П = absorption.

The content of the "Co–Mo–S phase" reaches a maximum for the optimum Co : Mo ratio. At low cobalt concentrations the fraction of this element entering into the composition of the "Co–Mo–S phase" is close to 100%; with increase of the cobalt concentration, the fraction falls and the content of the inactive sulphide $Co_9S_8$ increases.[42]

## 2. X-Ray Photoelectron Spectroscopic Data

The position of the Co2*p* level in the cobalt catalysts deposited on molybdenum sulphide is higher by 0.5 eV than in massive $Co_9S_8$.[46] The position of the Co2*p* peak for the remaining catalysts is close to that characteristic of $Co_2Mo_2S_4$. This led to the conclusion that the electronic states of cobalt in the "Co–Mo–S phase" and in $CoMo_2S_4$ are similar. Thus cobalt is present in the mixed catalysts in the form of Co(II) in a low-spin state. This interpretation of the XPES data differs from that proposed by Brinen and Armstrong,[61] who concluded that metallic cobalt is present in the sulphide catalysts. The study of the XPE spectra of $Co_9S_8$ [46] and $CoS_2$ [62] showed that the absence of satellite peaks is characteristic of the state of Co(II) in the sulphide systems.

## 3. EXAFS Data

According to EXAFS data,[48] only one peak on the radial distribution curve is observed for the oxide catalysts $Mo/Al_2O_3$ and $(Co+Mo)/Al_2O_3$. The absence of a second ordered coordination sphere shows that the coordination of the molybdenum ions in the catalysts investigated is greatly distorted. As a result of the conversion of the catalyst into the sulphide phase, more regular structures are produced. Comparison of the EXAFS data for $MoS_2$ and the sulphided catalyst led to the conclusion[48] that molybdenum ions enter into the composition of the dispersed $MoS_2$ particles, whose size is independent of the presence of cobalt in the catalyst. In the same study the authors concluded that oxygen ions are absent from the coordination sphere of molybdenum (i.e. the oxide sulphide groups are not formed in the system considered). The immediate environment of cobalt ions contains sulphur atoms and there is no order in the second coordination sphere of the cobalt ions. The Co–S distance in the "Co–Mo–S phase" differs from that between the same atoms in $Co_9S_8$ or $CoMo_2S_4$. The composition of the coordination sphere of cobalt changes when the catalyst comes into contact with air.

## 4. Infrared Spectroscopic Data

Bands corresponding to the hydroxy-groups of the carrier are not observed in the infrared spectra of the catalysts sulphided at 320 °C.[49] Such groups are manifested in the spectra of catalysts sulphided at 600 °C. This indicates the formation of three-dimensional sulphide particles when the catalysts are subjected to a high-temperature treatment, which is also confirmed by electron microscope data. It is believed[50] that the absence of bands due to the OH groups of the carrier from the infrared spectra indicates the retention in the catalysts subjected to a low-temperature treatment (320 °C) of the bond between the active component and the carrier (although the character of this bond remains undefined).

The use of NO as the probe molecule in the study of the surface compounds in the $(Co+Mo)/Al_2O_3$ oxide catalysts revealed the formation of a mixed compound (the "Co–Mo–O phase"). This compound can apparently be regarded as the precursor of the active component formed after treatment with sulphur.[30] The intensity of the absorption bands of the NO adsorbed on the "Co–Mo–O phase" was proportional to the activity of the sulphided catalyst. The amount of adsorbed nitric oxide is also correlated with the catalytic activity.[29] It is noteworthy that the structure of the "Co–Mo–O phase" differs from that of cobalt molybdate.

The infrared spectra of the adsorbed nitric oxide make it possible to distinguish two types of adsorption centres in the sulphided $(Co+Mo)/Al_2O_3$ catalysts—on molybdenum and cobalt.[54] It was found that, with the increase of the cobalt content in the catalyst, the number of adsorption centres containing Mo ions falls. A correlation has been observed between the catalytic activity and the amount of nitric oxide adsorbed on cobalt ions. This permitted the important conclusion that cobalt ions enter directly into the composition of the active centres.

## 5. The Structure of the Active Component of the $(Co+Mo)/Al_2O_3$ Sulphide Catalyst

The MES and EXAFS data are inconsistent with the oxide sulphide and intercalation models and also the synergistic model. On the basis of the set of data obtained, Topsøe

and co-workers[14,50,54] proposed a model, according to which the active component (the "Co–Mo–S phase") consists of highly dispersed particles having the $MoS_2$ structure (usually a single-layer packet). The cobalt atoms are present on the lateral faces of these packets. According to Candia et al.[54], the cobalt atoms block the coordination-unsaturated molybdenum ions distributed on the lateral face. A structure of the active component corresponding in essence to the Ratnasamy model[13] has been put forward by Topsøe et al.[40] For a high degree of dispersion of the active phase (sulphide particle size ~10 Å), the maximum concentration of cobalt ions distributed on the lateral force of the $MoS_2$ crystal can correspond to a stoichiometry with Co : Mo ≅ 0.5.[40] An increase of the cobalt content above the optimum value entails the formation of the inactive sulphide $Co_9S_8$. In conformity with the model proposed by Topsøe and co-workers,[14,50,54] the increase of the activity of the catalyst as a consequence of the deposition of cobalt is associated with the formation of new centres. The degree of dispersion of the molybdenum sulphide particles does not change when cobalt is introduced into the catalyst and the "Co–Mo–S phase" is formed.

## IV. CONCLUSION

The study of the (Ni +W)/$SiO_2$ and (Co +Mo)/$Al_2O_3$ catalytic systems of different composition by a combination of physical methods led various groups of investigators to similar conclusions concerning the nature of the active compounds in the hydrodesulphurisation catalysts: the active component in the sulphide catalysts consists of highly dispersed sulphide particles retaining the layer structure characteristic of the massive sulphides ($MoS_2$ or or $WS_2$); the active centres, incorporating the atoms of the second transition element (nickel or cobalt), are distributed on the lateral faces of the highly dispersed sulphides; the increased activity of the mixed catalytic systems is due to the formation of a surface compound containing the atoms of both transition elements. The atomic activity of the centres in the mixed catalysts is appreciably higher (apparently by about two orders of magnitude) than that of the centres in catalysts containing only one metal.

There is some discrepancy in the data obtained in the study of the above systems as regards the estimation of the degree of interaction with the carrier. For the (Ni +W)/$SiO_2$ catalysts obtained from organometallic compounds, there exist data demonstrating the retention of a bond between tungsten and the oxygen of the carrier. It may be that this is due to the method of preparation of the catalyst via the stage in which the organometallic complexes are fixed on the carrier. Oxygen atoms were not detected by the EXAFS method in the first coordination sphere of molybdenum in the (Co +Mo)/$Al_2O_3$ catalysts. However, one cannot rule out the possibility that a small number of chemical bonds between $MoS_2$ and the carrier are retained in this catalyst too, which is the reason for the retention of a high degree of dispersion of the deposited sulphides under severe conditions of the operation of the catalyst.

Thus important features of the active formations in the mixed sulphide catalysts were elucidated recently as a result of the application of a combination of physical methods. However, the role of the individual components of the catalyst remains obscure. Different causes of the promoting influence of Group VIII metals ($M^{VIII}$) added to Group VI metal ($M^{VI}$) sulphides have been discussed in the literature (see, for example, Pratt and Sanders[63]). These causes can be divided into two groups:

(1) The introduction of the metal $M^{VIII}$ leads to the structural modification (an increase of the degree of dispersion and stability) of the sulphide $M^{VI}S_2$;

(2) The introduction of the metal $M^{VIII}$ increases the number of the active centres in the $M^{VI}S_2$ phase (anionic vacancies, reduced $M^{VI}$ ions) as a result of the activation of hydrogen.

Data obtained by electron microscopy[22,32] have shown that the introduction of nickel into the W/$SiO_2$ catalyst can increase the degree of dispersion of the sulphide particles, but this is not the main cause of the sharp increase of the activity of the mixed catalysts. An increase of the degree of dispersion of the sulphide particles as a consequence of the introduction of cobalt has not been observed in the Mo/$Al_2O_3$ system.[54]

The study of catalysts obtained by depositing $Ni(C_3H_5)_2$ on massive tungsten disulphide has shown[28,29] that the activity referred to one nickel atom is approximately constant regardless of the nickel concentration and also of the morphology and area of the $WS_2$ surface. The same atomic catalytic activity is characteristic of deposited catalysts at low nickel concentratons (below the optimum value of λ). This suggests that nickel enters directly into the composition of the active centres. There exist different views concerning the ions ($M^{VI}$ or $M^{VIII}$) which constitute the centres for the activation of thiophen. A scheme for the hydrogenolysis of thiophen on the "Co–Mo–S phase", according to which thiophen is activated on molybdenum ions, has been put forward.[14] It has been suggested[14] that the presence of cobalt weakens the Mo–S bond, which facilitates the removal of sulphur under the reaction conditions with formation of coordination-unsaturated molybdenum ions on which thiophen is adsorbed. It has been concluded[54] that the active centres in the mixed sulphide catalysts incorporate directly the atoms of the Group VIII–VI element.

Analysis of the possible strength of the bonds between sulphur and surface centres of different composition has led to the hypothesis[36] that the active centre contains $M^{VIII}$ ions. The layer sulphide $M^{VI}S_2$ serves as a matrix for the stabilisation of $M^{VIII}$ in the sulphide environment. The role of the Group VI metal may also consist in altering the reactivity of the centre containing the $M^{VIII}$ ion (for example, in facilitating the removal of the sulphur bound to $M^{VI}$ as a result of the formation of the $M^{VI}$–$M^{VIII}$ bond).

Despite the fact that significant progress has been made in recent years in the elucidation of the nature of the active component in sulphide hydropurification catalysts, a whole series of questions concerning the mechanism of the action of these catalysts still awaits an answer. One of these questions is why a specific combination of two metals (namely the location of cobalt or nickel in the layer structures of tungsten or molybdenum sulphides) actually ensures a high activity in the hydrogenolysis of the C–S bond. The mechanism of the activation of the C–S bond and of the hydrogen molecule on sulphide catalysts remains unelucidated. Further studies should provide an answer to these questions and should also yield additional data on the structure of the active centres in one of the most important classes of industrial catalysts—the hydropurification catalysts.

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# The Application of Deuterium in the Study of Heterogeneous Organic Catalysis

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The use of deuterium for the study of the mechanisms of heterogeneous-catalytic organic reactions and of the adsorption of organic molecules on the surface, the structure of the active centres and properties of catalysts, as well as other aspects of catalysis is examined. The possibilities of employing data obtained by measuring the rate of deuterium exchange, by the analysis of the isotope distribution in the products, and by the determination of kinetic isotope effects are demonstrated. The bibliography includes 168 references.

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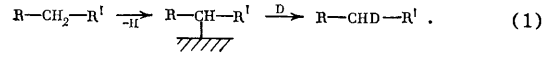
## I. INTRODUCTION

Increased attention to the reaction mechanism is a characteristic feature of present day studies in the field of heterogeneous catalysis. Among the numerous methods used to solve problems associated with this factor, the isotope methods, in particular those based on the use of deuterium, occupy a notable place. The employment of deuterium in catalysis began as early as the 1930s–1940s in the well known studies by the brothers Farkas, Grinev, and Polanyi. However, it began to be used widely and comprehensively only after the publication in the 1950s of a cycle of the fundamental studies by Kemball, which have since become classical.[1] Extensive literature data have been surveyed in the existing reviews[2-4], but the methodological procedures which assist in the determination of the mechanism of a particular heterogeneous-catalytic reaction by the introduction of the deuterium label have never been examined systematically. Nevertheless the number of studies on catalysis using deuterium has been growing continuously and the attempt at this kind of systematic account undertaken in this review has been fairly urgently needed. As a consequence of the limited space available in the review, we shall deal only with organic heterogeneous catalysis.

It is possible to differentiate three main methods of using deuterium in the study of organic heterogeneous-catalytic reactions: (1) measurement of the rate of deuterium exchange involving compounds participating in the reaction, frequently combined with its comparison with the rate of the main reaction of the compounds; (2) analysis of the isotope distribution in the initial reactants or the final products of the catalytic reaction; (3) measurement of the kinetic isotope effects when hydrogen is replaced by deuterium in one or several components of the reaction mixture. Depending on the specific features of the catalytic system investigated, each of these methods is used in different versions.

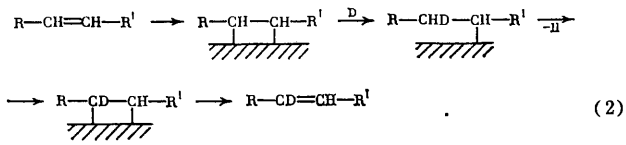
## II. RATE OF DEUTERIUM EXCHANGE

A heterogeneous-catalytic reaction is known to have more than one elementary stage. In the study of the reaction mechanism the queston of which stage is the slowest always arises. If hydrogen participates in the reaction, important information about this stage can be obtained by measuring the rate of deuterium exchange involving the initial compounds. A bond with a hydrogen atom must be broken in the deuterium exchange and a new bond must be formed with a deuterium atom. In the case of saturated hydrocarbons, the main pathway leading to the breaking of the C–H bond in deuterium exchange is dissociative adsorption on the catalyst:



(1)

For unsaturated compounds, there is yet another pathway, namely the addition of a deuterium atom to the multiple bond with formation of a semihydrogenated form and subsequent elimination of a hydrogen atom:



(2)

Since dissociative adsorption or the formation of the semihydrogenated form can occur as stages in other reactions of hydrocarbons, for example, in dehydrogenation or hydrogenation, comparison of the rates of deuterium exchange [processes (1) and (2)] with the rate of the given reaction investigated helps to establish the rate-limiting stage.

### 1. Determination of the Rate of Deuterium Exchange

Thus the problem arises of the correct estimation of the rate of deuterium exchange. If the reaction proceeds in a static system, Kemball's equations are used:[1]

$$k_0 = \frac{100 - d_{0,\infty}}{t} \ln \frac{100 - d_{0,\infty}}{d_0 - d_{0,\infty}}, \quad (3)$$

where $k_0$ is the initial rate of consumption of the non-deuteriated organic molecules, $d_0$ the fraction (as a percentage) of the non-deuteriated molecules at time $t$, $d_{0,\infty}$ their equilibrium fraction (as a percentage), and

$$k_\varphi = \frac{\varphi_\infty}{t} \ln \frac{\varphi_\infty - \varphi_0}{\varphi_\infty - \varphi}, \quad (4)$$

where $k_\phi$ is the number of deuterium atoms entering 100 molecules of the organic compound per unit time, $\phi = \sum_{i=1}^{m} i d_i$ ($d_i$ is the fraction of the organic molecules $C_mH_n$ containing $i$ deuterium atoms), $\phi_0$ is the initial value of $\phi$, and $\phi_\infty$ its

equilbrium value, defined by

$$\varphi_\infty = \frac{100n \cdot 2y}{n+2y}$$

($y$ is the ratio of the initial molar concentrations of $D_2$ and $C_mH_n$).

If the initial deuterium content in the organic molecule is zero ($\phi_0 = 0$), which is usually the case, the gaseous deuterium is present in the system in an excess so that $d_{0,\infty} \cong 0$, then Eqns.(3) and (4) simplify and become respectively

$$k_0 = \frac{100}{t} \ln \frac{100}{d_0}$$

and

$$k_\varphi = \frac{\varphi_\infty}{t} \ln \frac{\varphi_\infty}{\varphi_\infty - \varphi} \quad .$$

Having plotted $\ln d_0$ against $t$ and $\ln(\phi_\infty - \phi)$ against $t$, it is possible to find $k_0$ and $k_\phi$ respectively from the slopes of the straight lines.

It is seen from Eqn.(3) that $k_0$ has the dimensions of the reciprocal of time, i.e. it is a relative quantity indicating the fraction of the molecules (as a percentage) involved in the exchange per unit time. The rate of disappearance of non-deuteriated molecules can be obtained by multiplying $k_0/100$ by the concentration of the organic compound. The rate of incorporation of deuterium into organic molecules can be obtained in exactly the same way from $k_\phi$. The quantities $k_0$ and $k_\phi$ may not be identical because several hydrogen atoms of one organic molecule can be substituted by deuterium simultaneously. The ratio

$$M_D = k_\varphi / k_0 \qquad (5)$$

characterises the multiplicity or extent of the exchange, i.e. the number of D atoms entering one organic molecule per reaction step.

Isotope exchange is a first-order reaction with respect to the isotope,[5] i.e. in any specified initial mixture involved in deuterium exchange in the static system the rate of consumption of the hydrogen-containing molecules on all gaseous deuterium is described by the first-order Eqn.(3). At the same time the form of the kinetic equation describing the rate of deuterium exchange as a function of the concentration of the reaction components is determined by the mechanism of a specific process. The rate of exchange usually increases with increasing concentration of hydrocarbon molecules, while an increase in the deuterium concentration entails a retardation of the exchange.[2]

The estimation of the rate of deuterium exchange in a flow-circulation system has certain specific features. In contrast to the usual reactions where a chemical transformation takes place, in deuterium exchange a molecule which has reacted once is not "removed from play" and can undergo new isotope exchange steps. The experimental degree of reaction (exchange) is then too low. In the usual formula for the calculation of the rate of reaction in a flow-circulation system one therefore introduces a correction which takes into account the possibility of such repeated exchange:[6]

$$r_{об} = \frac{u_0 x_{exch} M_{av}}{g M_D} \quad ,$$

where $u_0$ is the flow rate of the exchanging molecules, $x_{exch} = (100-d_0)/100$ the degree of exchange, $g$ the weight of the catalyst sample, $M_{av}$ the average number of D atoms in the exchanging molecules after the experiment, and $M_D$ the number of D atoms entering one molecule in one exchange step.

The quantity $M_{av}$ can easily be determined from the results of the mass-spectrometric analysis of the products and $M_D$ can be found from Eqn.(5). One must bear in mind in the calculation of $k_\phi$ and $k_0$ in Eqn.(5), that the quantities $d_0$ and $\phi$ are determined in the given instance at only two points—the initial point and the time $t$, and the accuracy of the estimate can therefore be low. In order to improve the accuracy, one can set up special experiments, but the rate of exchange and the rate of the main reaction usually differ sufficiently and there is no doubt which of these processes predominates.

The methods for the determination of the rate of exchange when the molecule contains hydrogen atoms which are not equivalent as regards reactivity are described below.

## 2. The Use of Data for the Rate of Deuterium Exchange

In the first place we shall consider specific examples where information about the mechanism of the catalytic reaction can be obtained by comparing its rate with that of deuterium exchange.

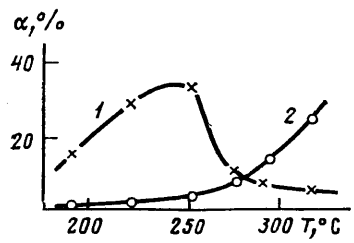



**Figure 1.** Temperature dependence of the degrees α of exchange involving cyclohexane (curve *1*) and of its dehydrogenation (curve *2*) on the nickel catalyst.[7]

The mechanism of the dehydrogenation of cyclohexane and the related benzene and cyclohexene hydrogenation reactions on a nickel catalyst has been investigated[7] with the aid of deuterium. It was found that the deuterium exchange involving cyclohexane begins at a lower temperature and is much faster than its dehydrogenation. However, with increase of temperature, the rate of dehydrogenation (which in the given case, in a flow-circulation system, is proportional to the degree of reaction) increases and the rate of exchange falls after passing through a maximum (Fig.1), so that dehydrogenation now becomes the faster process. The high rate of deuterium exchange at the beginning of the experimental temperature range evidently demonstrates that the dissociative adsorption stage, which is common to both reactions, cannot limit the rate of dehydrogenation. An increase of temperature promotes a further reaction (dehydrogenation) of the dissociatively adsorbed cyclohexane and the suppression of the competing process involving its desorption with substitution of the eliminated H atoms by D (i.e. the deuterium exchange is retarded). This entails the reversal of the ratio of the rates of the exchange process and the cyclohexane dehydrogenation reaction. A similar phenomenon has been observed also in the deuterium exchange involving a series of paraffinic hydrocarbons on nickel under the conditions of hydrogenolysis and dehydrocyclisation.[8]

The rate of deuterium exchange involving the potential intermediate of this reaction, namely cyclohexene, is extremely low under the same conditions and is much lower than the rate of its hydrogenation.[7] Presumably the adsorption of cyclohexene (probably with dissociation of the double bond) is in this instance virtually irreversible and the intermediate surface compound formed reacts further rapidly.

The deuterium exchange involving benzene, which has been investigated in both flow-circulation[7] and static[9] systems, is faster than the hydrogenation of benzene. However, comparison of the temperature variations of the rates of both reactions (Fig. 2) shows that they proceed independently via different surface intermediate species.

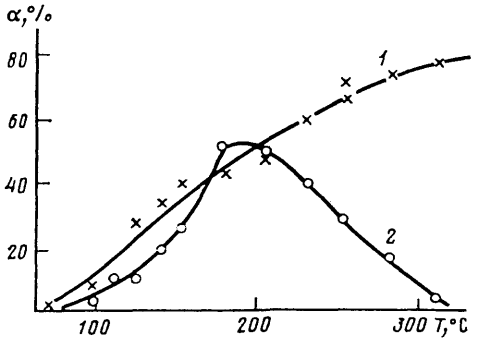



Figure 2. Temperature dependence of the degrees α of exchange involving benzene (curve *1*) and of its hydrogenation (curve *2*) on the nickel catalyst.[7]

Analysis of the relations obtained using kinetic, adsorption, and other data made it possible to develop a fairly convincing general mechanism of the reactions in the benzene–cyclohexane system on a nickel catalyst.[7] Analogous conclusions have been reached by comparing the rates of exchange and deuteriation also for the reaction with participation of toluene.[10]

One may point to a series of other studies in which comparison of the rates of deuterium exchange and a chemical reaction yielded valuable information about the mechanisms of the processes investigated. Such data have been obtained for the hydrogenation of ethylene on $Al_2O_3$,[11] propene on rhodium,[12] isoprene on palladium,[13] benzene on a series of metals,[14] and mesityl oxide on palladium,[15] for the hydrogenation of a series of alkanes on titanium dioxide,[16] n-decane on alumir.oplatinum[17] and platinum–tin[18] catalysts, and isopentene on the calcium–nickel–phosphate catalyst,[6] for the conversion of cyclohexanol into cyclohexanone on a copper–magnesium catalyst,[19] for the hydrogenolysis of thiophen on an industrial aluminonickel–molybdenum catalyst,[20] for the hydrogenation and isomerisation of hexenes on "sulphided" palladium,[21] for the hydrogenolysis and isomerisation of propane and butane on platinum[22] and n-pentane on nickel, platinum,[23] and platinum–lead and platinum–copper catalysts,[24] for the hydrogenolysis and dehydrogenation of cyclohexanes on platinum and nickel,[25] for the *cis–trans* isomerisation and migration of the double bond in butenes on nickel,[26] and for a number of other processes.

The measurement of the rate of deuterium exchange involving not only the starting materials but also the reaction products can also be of considerable interest. Thus the high rate of exchange involving the methane formed in the hydrogenolysis of hydrocarbons on sputtered iron films[27] and on rhodium–iridium catalysts[28] made it possible to reject the hypothesis that the rate-limiting stage in this reaction is the desorption of its products. However, there exist also contradictory data according to which the rate of hydrogenolysis of hydrocarbons on iridium, rhodium, ruthenium[29,30] and on palladium–silver alloys[31] is determined precisely by the rate of the desorption stage.

The rate of deuterium exchange is not measured solely in order to compare it with the rate of the chemical reaction investigated to establish the process mechanism. Deuterium exchange has proved to be a sensitive instrument for the investigation of the catalysts themselves. By estimating the influence of the composition of the catalyst, of the degree of its dispersion and its genesis, of its treatment by various substances, etc., on the rate of deuterium exchange, it is possible to obtain information about the nature, structure, and properties of the active centres of the catalysts. Thus it has been possible to establish with the aid of deuterium exchange involving ethylene that the active centres of catalysts containing chromium in a magnesium oxide matrix are $Cr^{2+}$ ions.[32] Deuterium exchange has been used also to investigate a series of other oxide catalysts.[33–36] Measurement of the rate of deuterium exchange involving hydrocarbons made it possible to elucidate the way in which the temperature of the preliminary treatment influences the activity of $\gamma$-$Al_2O_3$ [37] and barium oxide[38] and to obtain data on the active centres in these catalysts.

In many studies the active centres have been investigated by treating the catalysts with various substances, mainly sulphur-containing substances, which influence the rate of deuterium exchange and other reactions of organic molecules. The unequal effects of the treatment of molybdenum sulphide with hydrogen sulphide on the hydrogenation of ethylene and on the exchange between the latter and $C_2D_4$ led to the conclusion that two types of active centres exist on the surface of this catalyst[39] and differ in the degree of coordination unsaturation of the molybdenum atoms.[40] Similar data have been obtained also for nickel sulphide.[41] Different active centres, responsible for the isomerisation of n-butene and for the deuterium exchange involving benzene and n-butene, have been detected also on the surface of alumina: the former incorporate $Al_2^{3+}$ and sometimes also $O_2^-$ and the latter incorporate $O_2^-$ ions differing from those participating in isomerisation.[42] The influence of the poisoning of the $Pt/Al_2O_3$ catalyst with hydrogen sulphide, sulphur dioxide, and other poisons on the hydrogenation, hydrogenalysis, and deuterium exchange reactions of certain hydrocarbons.[43,44]

Investigation of the dependence of the rate of deuterium exchange involving ethane,[45] cyclopentane,[46] and cyclohexane[47] on the degree of dispersion of platinum led different investigators to different conclusions, so that the question of the structural sensitivity of these reactions remains controversial. The assignment of the reaction to a particular type is believed[48] to depend on the degree of reaction and, after the attainment of complete surface coverage of the catalyst, the structure-sensitive reaction can become "structure-insensitive". Doubt have been cast on the validity of the usual methods for the determination of the structural sensitivity of catalytic reactions on metals[49] in view of the results of the study of the deuterium exchange involving 2,2-dimethylbutane on platinum and palladium.

The rate of deuterium exchange involving benzene proved to be different on different crystallographic faces of a platinum single crystal,[50] in contrast to the rate of its hydrogenation, which constitutes an additional argument in support of the view that the mechanisms of these reactions are different.[7]

The measurement of the rate of deuterium exchange involving hydrocarbons is used particularly widely in comparisons with the rates of other reactions, in the study of bimetallic catalysts. This usually makes it possible to estimate the role of the cluster and ligand effects in such systems.

It has been postulated[51-54] and confirmed by calculation[55] by Dalmon's method[56] that deuterium exchange takes place in clusters smaller than those required for hydrogenolysis. The fact that the rate of hydrogenolysis of hydrocarbons (dissociation of C–C bonds) depends more strongly on the composition of nickel–copper[51-53] and platinum–gold[54] alloys than the rate of deuterium exchange (dissociation of C–H bonds) has been interpreted as evidence for the decisive role of the size of the *ensembles*, i.e. of the geometrical factor, in these and similar systems. However, in subsequent studies using deuterium exchange involving cyclohexane and n-hexane on nickel–copper alloys,[55] ethane and neopentane on ruthenium–copper and ruthenium–silver alloys,[57] and methane and neopentane on palladium–gold alloys[58] it was emphasised that, together with the geometrical factor, account must be taken also of the electronic factor. It is appropriate to mention, if only selectively, also certain other studies in which deuterium exchange involving various hydrocarbons has been used to investigate the catalytic properties of Pt–Re,[56-60] Pt–Ir, Ir–Os,[60] Pt–Pd,[61] Pd–Ni,[62] Ni–Mo,[63,64] Ni–Cu,[65] and Pd–Ag [31] alloys. The isotope exchange between methane and deuterium has been suggested as a method for the determination of the composition of the surfaces of platinum–palladium alloys.[61]

Finally the measurement of the rate of deuterium exchange can be used to estimate the strength of the C–H bonds and the reactivities of the hydrogen atoms in various groups in organic molecules. It was found that the rate of deuterium exchange in a series of cycloalkanes is correlated with the "bond indices" calculated by quantum-chemical methods and characterising the strength of the C–H bonds after adsorption on nickel.[66] The reactivities of all the hydrogen atoms in cycloalkanes are approximately equal, which follows from the linearity of the relation plotted in terms of the variables of Eqn.(4) over a fairly wide range of degrees of exchange. However, there are many compounds in the molecules of which the hydrogen atoms are not equivalent. Such non-equivalence leads to a break in the straight line plotted in terms with the variables of Eqn.(4), as shown for toluene in Fig. 3.

A method is known whereby it is possible to determine separately the rate of exchange in each group.[67] For the initial section of the curve illustrated in Fig. 3, the quantity $k_\phi = k_A + k_B$, which corresponds to the overall rate of exchange in groups A and B, is found by equations of type (4). The second section of the curve, beyond the break, corresponds to the exchange of hydrogen in the less reactive group B (the exchange in group A has already terminated by this time). The constant $k_B$ for the second group of atoms can be found from the second section by means of the equation

$$k_B = \frac{\varphi_{B,\infty}}{t} \ln \frac{\varphi_{B,\infty} - \varphi_0}{\varphi_\infty - \varphi} .$$

However, for this purpose, it is necessary to know the quantity $\phi_{B,\infty}$ which corresponds to $\phi_\infty$ but refers only to the second group. The quantity $\phi_{B,\infty}$ is calculated from the relations

$$\varphi_\infty = \varphi_{A,\infty} + \varphi_{B,\infty} ,$$

$$\varphi_{A,\infty}/\varphi_{B,\infty} = n_A/n_B ,$$

where $n_A$ and $n_B$ are the numbers of hydrogen atoms in groups A and B respectively. The quantities $n_A$ and $n_B$ are found by analysing the molecular structure and the dynamics of the time variation of the concentrations of the various deuterio-products.[68] Thus it is possible to determine the rate of deuterium exchange in each of the groups A and B.

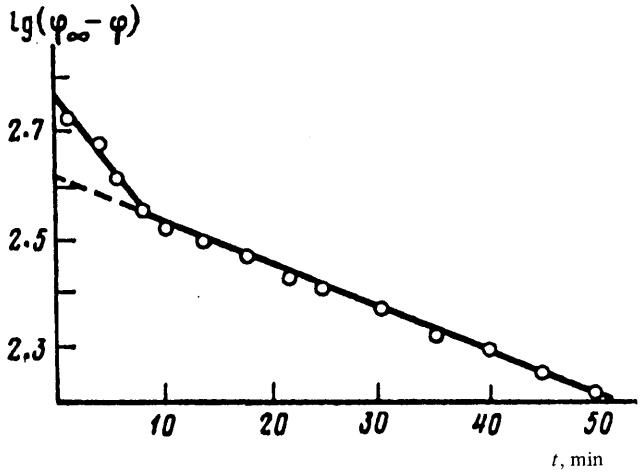



**Figure 3.** Time variation of the rate of deuterium exchange involving toluene in terms of the variables of Eqn.(4).[68]

The rates of exchange of the hydrogen atoms in the ring and in the side groups in alkylbenzenes have been measured by this procedure.[68,69] It is of interest that, whereas the rate of hydrogenation varied consistently as a function of the positions and numbers of the alkyl substituents, the rate of exchange within each group (in the ring and in the substituents) remained fairly constant for the entire series of compounds investigated. Correlations between the rate of exchange and the quantum-chemical quantities characterising the average population of the C–H bonds after the adsorption of hydrocarbons on nickel were found from these data:[70] the higher the population, the lower the rate of exchange.

The unequal reactivities of the α- and β-hydrogen atoms in the thiophen molecule[71] and of the hydrogen atoms in the methyl, methylene, and methylidyne groups in saturated hydrocarbons[72] were demonstrated in a similar way.

## III. ISOTOPE DISTRIBUTION

The determination of the isotope distribution in the reaction products is a widely used procedure, which is at the same time difficult to subject to a formal treatment. It is used in the study of catalytic processes involving deuterium. In each specific case different aspects of the distribution can be of greatest interest: the type of exchange (simple or multiple) in the initial and final products and the possible intermediates, the most probable site where deuterium enters the molecule, the dependence of the distribution

on the molecular structure, reaction temperature, other conditions, etc.

We shall examine initially the possibilities for the theoretical calculation of the isotope distribution in deuterium exchange products.

## 1. Calculation of the Distribution

Deuterium–hydrogen exchange processes are usually subdivided into simple and multiple. In the former case one hydrogen atom is substituted by deuterium in each reaction step and the quantity $M_D$ calculated by Eqn.(5) is unity. When $M_D > 1$, the occurrence of multiple exchange is indicated, where more than one hydrogen atom is replaced by deuterium in at least some of the molecules. When the molecule contains only equivalent hydrogen atoms, the simple exchange is a statistical process and is readily susceptible to calculation. Up to a certain degree of exchange $x$, the fraction of each isomer $d_i$, whose molecule contains $i$ deuterium atoms, can be found from the formula[73]

$$d_i = \frac{n!}{i!\,(n-i)!}\, x^i (1-x)^{n-i} \quad , \qquad (6)$$

where $n$ is the number of hydrogen atoms capable of exchange and $x$ the average fraction of hydrogen atoms in the hydrocarbon molecules substituted by deuterium. However, there exist compounds whose molecules contain groups of hydrogen atoms which are not equivalent as regards reactivity. Although the exchange in each group can be of the simple type, nevertheless one must not calculate the overall distribution of the deuterioisomers by Eqn.(6) in this instance. For such compounds, a method of calculating the distribution,[74] based on the statistical analysis of the independent exchange processes in two different groups A and B, has been developed. Agreement between calculated and experimental distributions is achieved by selecting the appropriate ratio of the rates of deuterium exchange in these groups $k_A/k_B$. If reliable independent evidence showing that the exchange does in fact proceed via a non-equivalent substitution mechanism is available, then $k_A/k_B$ can be calculated from the distribution data, i.e. the relative reactivities of different hydrogen atoms in a given process can be estimated quantitatively as a function of the process conditions.[74,75]

The situation is much more complex as regards the theoretical calculation of the distribution in multiple deuterium exchange. Attempts at such a calculation have been made,[76–79] but they are all based on an artificial selection of parameters, which are not determined directly from experimental data; their value is therefore fairly limited.

Another approach, namely the kinetic approach, has been used by Nekrasov et al.[80] The study of the kinetics of deuterium exchange makes it possible to find a series of rate constants $k_n$ for the formation of products with the composition $d_n$. Taking into account the statistical probabilities of the formation of the exchange products of the initial molecule $d_0$ and from molecules which have already been partly substituted, it is possible to derive an expression for the rate of formation of any deuterium-substituted molecule $d_n$, which assumes the following form when the molecule contains, for example, 12 equivalent hydrogen atoms:[80]

$$r_n' = k_n d_0 + \sum_{i=1}^{n-1} C_{12-i}^{n-i} \sum_{m=0}^{i} \frac{C_i^m}{C_{12}^{n-i+m}}\, k_{n-i+m} d_i \quad ,$$

where the symbol $C$ denotes the number of combinations. The equation for the rate of consumption of deuterium-substituted molecules can be obtained similarly:

$$r_n'' = \left( k_0 - \sum_{i=1}^{n} k_i C_n^i / C_{12}^i \right) d_n \quad .$$

The observed rate of accumulation of each product containing $n$ deuterium atoms is defined by the expression

$$r_n = r_n' - r_n'' \quad .$$

Knowing the constant $k_n$, the concentrations of all the deuterium-substituted products at any instance can be calculated by means of these equations. The experimental distribution of the products of the deuterium exchange involving cyclohexane on nickel[80] and platinum[81] agrees satisfactorily with the calculated distribution.

The distribution, redistribution, and transfer of isotopic atoms both in the "pure" exchange and under the conditions of the occurrence of another accompanying reaction have been subjected to mathematical analysis in a general form in a series of investigations.[82–85] Unfortunately this analysis has not so far found application in research, possibly because of its complexity.

## 2. The Use of Isotope Distribution Data

As can be seen from the foregoing discussion, analysis of the isotope distribution is of a specific character in each case and it is extremely difficult to achieve a general classification of the procedures used for this purpose. One can only conclude that the character of the distribution in deuterium exchange usually serves as an indication of a particular form of adsorption of the test compound. Simple exchange, which is typical for oxide catalysts, occurs in one-point adsorption, while multiple exchange, which is more characteristic of metals, presupposes multipoint adsorption.[86] Incidentally, both simple and multiple exchange can take place on metals depending on the size of the *ensembles*.[87] A noval concept concerning the mechanism of the deuterium exchange involving alkanes and alkenes on metals, based on the hypothesis of the formation of intermediates of the carbene type, has been recently proposed by Dolgoplosk and co-workers.[88]

It was already stated above that a monotonic isotope distribution curve is as a rule observed in those cases where the hydrogen atoms are approximately equivalent as regards their reactivities.[7,13,19,23,89] On the other hand, if the hydrogen atoms can be subdivided into separate groups differing in their positions in the molecule and reactivities, characteristic deviations from monotonic variation appear on the distribution curve, which has been observed, for example, in the exchange involving methyl-substituted aromatic molecules,[10,67–69] cyclohexane,[80,81] and other compounds.[20,51,72,75,90] Incidentally, one should exercise a certain amount of caution as regards this problem, because the non-uniformity of the distribution can be caused in some cases also by purely kinetic factors (for further details about this, see Vlasveld and Ponec[62] and Nekrasov et al.[81]).

Among the characteristics of deuterium exchange of more or less general importance, one may name also the lower degree of exchange involving unsaturated compounds compared with the related saturated hydrocarbons.[4,6,13,91] It is of interest that the deuteriation of olefins is usually accompanied by the appearance in the initial instant of the reaction of a considerable amount of saturated molecules with the composition $d_0$ and $d_1$,[4,91–93] although the simple insertion of deuterium in the double bond should have yielded

only $d_2$ molecules. This can be explained by the slowness of the dissociative adsorption of deuterium in the presence of unsaturated compounds and also by the addition to the adsorbed molecule of the protium evolved in the dissociative adsorption of other hydrocarbon molecules,[4] i.e. by the redistribution of hydrogen.

We shall now proceed to the consideration of specific examples illustrating the possibility of employing hydrogen isotope distribution data for the elucidation of the mechanisms of catalytic reactions.

The study of the thiophen hydrodesulphurisation reaction yielded fairly unexpected results, which led the authors[94] to the conclusion that the hydrogen sulphide evolved in the presence of deuterium does not have the composition $D_2S$, as should have been the case when sulphur is abstracted by deuterium, but $H_2S$. This served as a basis for the hypothesis of an intramolecular mechanism of this reaction, according to which the dissociation of the C–S bonds is followed by the addition to the sulphur atom of the less mobile β-hydrogen atoms of thiophen and the "external" hydrogen (deuterium) is consumed only in the hydrogenation of hydrocarbon residues. This hypothesis was, as it were, supported by data for the isotope composition of the hydrogen sulphide in the deuteriolysis of thiophen containing deuterium in the α-positions and hydrogen in the β-positions.[20] Examination of the mass spectrum also demonstrated in this instance that mainly hydrogen sulphide having the composition $H_2S$ is formed in the reaction. However, subsequent careful investigation under conditions including also low degrees of reaction, in which the very first portions of the hydrogenolysis products evolved were analysed, demonstrated that the conclusion concerning the intramolecular mechanism was incorrect.[95] In fact the main sulphur-containing product of the deuteriogenolysis of thiophen on five different hydrodesulphurisation catalysts proved to be $D_2S$. This was confirmed also by the analysis of the isotope composition of the products of the hydrogenolysis of perdeuteriothiophen. The intense mass-spectrometric peak corresponding to a mass number of 34 (which formally corresponds to the mass of $H_2S$) was indeed observed, but it was of secondary origin. Its appearance is probably associated with the hydrogenolysis of the thiophen decomposition products, because an increase in the degree of hydrogenolysis entails also an increase in this peak. The above example demonstrated the necessity to resort to the greatest possible amount of additional evidence in assessing the isotope distribution data.

Another example is associated with the skeletal isomerisation of n-pentane. The results of a kinetic study of this reaction suggested that it involves hydrogen, although the latter does not enter into the stoichiometric equation. As a test, the isomerisation of n-pentane on a platinum catalyst was carried out in the presence of deuterium.[23] It was found that the reaction product (isopentane) contains significantly more deuterium than was present in the initial n-pentane. This effect was shown even more strikingly on platinum–lead and platinum–copper catalysts.[24] These results served as important evidence in support of the hypothesis of the direct involvement of hydrogen in skeletal isomerisation. Similar evidence indicating the participation of hydrogen has also been obtained by the deuterium exchange method for the double bond migration reaction[96] and the *cis–trans* isomerisation of hydrocarbons.[96,97]

There are reactions which cannot be detected at all without an isotope label because of the identity of the chemical properties of the initial reactants and final products. Thus the metathesis of olefins, for example of propene:

$$2CH_3{-}CH{=}CH_2 \rightarrow CH_3{-}CH{=}CH{-}CH_3 + CH_2{=}CH_2, \quad (7)$$

must inevitably be accompanied also by a process in which the methylene group is replaced not by an ethylene group but by a methylene group from another molecule. The replacement of some of the molecules of normal propene by the deuteriated analogues makes it possible to detect this "degenerate" or "latent" metathesis:

$$CH_3{-}CH{=}CH_2 + CD_3{-}CD{=}CD_2 \rightarrow CH_3{-}CH{=}CD_2 + CD_3{-}CD{=}CH_2. \quad (8)$$

Furthermore, the metathetical reaction of ethylene, in which products of a different chemical composition cannot be formed in principle, becomes accessible to observation:[98–100]

$$CH_2{=}CH_2 + CD_2{=}CD_2 \rightarrow 2\,CH_2{=}CD_2, \quad (9)$$

The appreciable difference between the rates of the explicit and latent metathesis of propene [reactions (7) and (8)] compared with the rate of reaction (9) served as important evidence[100] in support of the view that the reaction proceeds under the conditions of heterogeneous catalysis via a carbene chain mechanism, which has been proved for homogeneous systems.[101] Deuterium-labelled olefins have been used also in the metathetical reaction for the study of its stereospecificity[102,103] and its relation with the isomerisation reaction[104,105] and also for the determination of the mechanism of the formation of the intermediate carbene complex.[106]

Not only the isotope distribution in the products as such but also the position of the deuterium atoms in the molecule is important for the elucidation of the mechanism of this and other reactions. The isotope distribution, i.e. the relative contents of different deuterium-containing molecules, is usually determined mass-spectrometrically, most frequently by analysing the spectrum of molecular ions. Other methods, including microwave spectroscopy,[12,107–110] NMR,[111–118] and infrared spectroscopy[19] are used to determine the location of deuterium atoms in the molecule.

The study of the detailed distribution of deuterium yielded valuable information about the mechanism of the isomerisation of hydrocarbons,[107,108,110] the hydrogenation of propene,[118] butadienes,[116] cyclopentene,[115] substituted cyclohexenes,[112] various ketones,[117] and ethers,[114] the selective hydrogenation of dimethylethynylmethanol,[111] the dehydrogenation of cyclohexanol,[19] and other reactions.[109,113]

However, in certain cases mass-spectromatic analysis also provides certain definite possibilities for the determination of the position of the deuterium atoms. The point is that the mass spectrum usually represents not only molecular but also fragment ions formed as a result of the abstraction of entirely definite groups, for example, methyl groups from the molecule. Comparison of the isotope compositions of the molecular and fragment ions can yield some information about the part of the molecule in which deuterium atoms are preferentially located. For example, Fig. 4 shows that the isotope distribution of the fragment ions of *cis*-1,2-dimethylcyclohexane, formed by the abstraction of one methyl group, exactly reproduces the distribution of the molecular ions and that characteristic breaks in the monotonic variation of one curve correspond to analogous breaks in the monotonic variation of the other.[119] Since the difference between the mass numbers of these characteristic points is 18, the implication is that the hydrogen in the abstracted methyl groups has been fully replaced by deuterium, i.e. that they have the composition $CD_3$. The difference between the isotope compositions of the methyl groups in *cis*- and *trans*-1,2-dimethylcyclohexanes observed from the mass spectra[97] served as confirmation of the hypothesis that the molecules are arranged in different ways on the catalyst surface.

Comparative analysis of the mass spectra of the molecular and fragment ions of 5-methylfurfural and the products of its simultaneous decarbonylation and hydrogenation, 2-methylfuran and 2,5-dimethylfuran respectively, made it possible to determine the way in which the molecules are adsorbed on the palladium catalyst and to elucidate important details of the reaction mechanisms.[120] A similar approach has been used also to separate the hydrogen atoms of ethylbenzene into groups differing in their reactivity.[68]

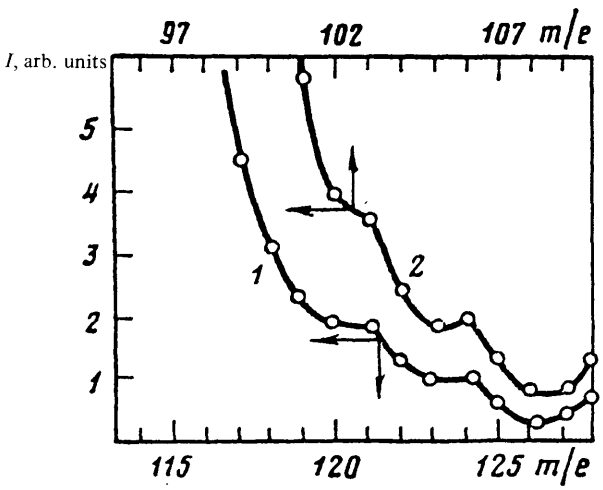



**Figure 4.** Isotope distribution of the products of the deuterium exchange involving *cis*-1,2-dimethylcyclohexane on platinum:[119] the intensities *I* of the peaks of the molecular (*1*) and fragment (*2*) ions.

Sometimes the intensity of the molecular ion peaks is so low that the isotope composition must be wholly estimated from fragment ions.[19]

One of the widely used procedures in isotope investigations involves the study of the reactions of certain compounds on the surface of a catalyst subjected to a preliminary treatment with deuterium. Information about the active centres on alumina catalysts,[121–125] niobium hydride,[126] molybdenum disulphide,[127] aluminosilicates,[122] and zeolites[128] has been obtained by this procedure. Evidently, this method is particularly useful for the study of catalysts with acid or basic centres but it is also useful in the study of the mechanisms of reactions on metals. Thus it has been shown[129,130] that intense deuterium exchange involving benzene takes place in the absence of deuterium from the gas phase on the surface of a nickel catalyst saturated with deuterium, but deuteriation hardly occurs.

Only after the introducton of deuterium into the gas phase, is the rapid formation of cyclohexane observed. Consequently hydrogen in a molecular form must participate in the benzene hydrogenation reaction, while in deuterium exchange it is involved in an atomic form, which confirms the mechanism proposed previously.[7]

There exist many other examples of the use of isotope distribution data for the investigation of the mechanisms of catalytic processes. We shall mention only some of them. Comparison of the observed calculated isotope distributions of the products on the hypothesis of a particular mechanism has been suggested[131] as a procedure for the determination of the rate-limiting stage of a process consisting of a series of parallel-consecutive reactions. The calculated and observed distributions have also been compared in the study of the hydrogenation of methylacetylene on platinum-group metals:[132] complete agreement between the calculated and experimental data has been noted only for reactions on palladium, platinum, and nickel.

Isotope distribution data have led to conclusions about the associative mechanism of the hydrogenation of methylene on magnesium oxide[133] and the involvement of dissociatively adsorbed intermediates in olefin hydrogenation reactions on the $Al_2O_3$ catalyst[134] and in their isomerisation on iron.[135] Data have also been obtained for the mechanisms of the selective hydrogenation of conjugated dienes,[91,136] the hydrogenation[137–139] and isomerisation[139,140] of olefins, the hydrogenolysis of paraffins,[141,142] and the dehydrogenation of n-decane[17,18] and isobutane[143] on platinum catalysts. A not altogether usual instance of the slow exchange involving a saturated hydrocarbon (isobutane) on a metal up to a fairly high temperature (400 °C) and conversely a rapid exchange involving an olefin (isobutene) has been observed.[143] These data and also comparison of the isotope distributions in the initial and final products led to the conclusion that the dissociative adsorption cannot be the slow stage of the dehydrogenation reaction in this instance.

Analysis of the isotope distribution in the methane and ethylene formed when carbonaceous deposits on the $Co/Al_2O_3$ and Co/C catalysts are treated with deuterium showed that they include both the $CH_2$ fragments and carbide carbon.[144] The adsorption-chemical equilibrium involving methane on nickel has been studied by a similar procedure with the aid of perdeuteriomethane.[145]

## IV. KINETIC ISOTOPE EFFECT

Measurement of the kinetic isotope effect (KIE) is the simplest way of using deuterium for the study of catalytic reactions. Here there is no need to determine the isotope composition and hence there is no need to employ the mass-spectrometric or another complex analytical method. One compares the rate of the reaction with participation of the usual reactants with its rate after the replacement of hydrogen by deuterium in one or several components or in specific sites in the initial molecule: the non-identity of these rates indicates the involvement of the corresponding hydrogen atoms in the slow stage of the reaction. However, in practice the measurement of the KIE is associated with certain difficulties.

The theory of kinetic isotope effects in homogeneous systems has been fairly highly developed,[146] which unfortunately cannot be said of heterogeneous-catalytic processes. This is not an appropriate place for the consideration of the theoretical aspects of the problem and it is sufficient to say that, in the measurement of the KIE in heterogeneous catalysis, one may encounter, apart from the trivial experimental errors associated, for example, with the different degrees of purification of the deuteriated and non-deuteriated reactants, also difficulties due to the incorrect estimation of the reaction rates, the deactivation of the catalyst, the influence of side processes, an incorrect interpretation of the reverse effects, their dependence on temperature, etc.

The kinetic isotope effect is characterised by the ratio $\beta$ of the rates of the processes occurring with participation of the light and heavy isotopes under identical conditions and for the same composition of the reaction mixture (for identical degrees of reaction):

$$\beta = r_H/r_D .$$

If the kinetic equation for the reaction is known and the rate constants involved in it has been determined for the reactions with participation of hydrogen and deuterium, then the constancy of the degree of reaction is not an obligatory condition, because the rate of reaction can be easily calculated for any composition. However, as a rule, such data are not available and the failure to meet this requirement may be a source of errors. In the case of kinetic power equations the ratio of the rates is equal to the ratio of the rate constants.

The reverse values of the KIE, i.e. the increase and not the decrease of the rate of reaction following the replacement of the light isotope by the heavy isotope, at first sight conflict with the elementary theory of isotope effects based on the transition state method.[146] This phenomenon has been explained[147] by the multistage nature of the hetereogeneous-catalytic processes and the swamping of the decrease of the rate in the slow stages by the shift of the equilibrium in the fast stages, including the adsorption and desorption stages, and also by the specific shift of the zero-point energy levels of the activated complexes in the slow stages on isotope substitution. We may note that, in principle, one cannot rule out the complete compensation of the forward effect by the reverse effect, which would outwardly appear as the absence of a KIE. It is therefore useful to carry out measurements under different conditions by altering, for example, the temperature.

The true KIE, i.e. the change in the rate constant for the slow stage after the replacement of one isotope by another, can be masked by the thermodynamic effects of the preceding fast stages. The change in the contribution to the overall process by side reactions whose rates are different in the presence of hydrogen and deuterium can also be reflected in the observed KIE for the reaction investigated.[148]

As a result, for the same reaction under similar conditions, different investigators have frequently obtained markedly different values of the KIE. Thus in a study of the hydrogenation of benzene on the $Ni/SiO_2$ catalyst at 240 °C, measurements were made of the rates of the following reactions:

$$C_6H_6 + 3H_2 \xrightarrow{r_1} C_6H_{12},$$
$$C_6H_6 + 3D_2 \xrightarrow{r_2} C_6H_6D_6,$$
$$C_6D_6 + 3D_2 \xrightarrow{r_3} C_6D_{12},$$
$$C_6D_6 + 3H_2 \xrightarrow{r_4} C_6H_6D_6.$$

The following values of the KIE were obtained: $r_1/r_2 = 0.60$, $r_1/r_4 = 0.53$, $r_4/r_3 = 0.55$, and $r_1/r_3 = 0.28$. On the other hand, in another study[149] the KIE obtained on a similar catalyst at 85 °C were respectively 0.7, 1.1, 0.8, and 0.9. Evidently the discrepancies are fairly considerable, particularly for the ratio $r_1/r_4$ and $r_1/r_3$. This may be partly associated with the difference between the temperatures; for example, according to Kiperman et al.[7], the ratio $r_1/r_2$ changed from 0.60 to 0.51 when the temperature increased from 240° to 270 °C. If the comparison has been made solely on the basis of only one ratio, for example $r_1/r_4$, then the results obtained in the two studies[7,149] might have led to opposite conclusions. The authors' interpretations in the two cases are based on fairly extensive experimental data and the role of random conclusions is reduced to a minimum. One can therefore assume that at 240 °C, i.e. in the region where the reaction is reversible, the ratio of the rates of the individual stages is different than at 85 °C, where "pure" hydrogenation takes place.

In the reverse reaction involving the dehydrogenation of cyclohexane, the replacement of hydrogem by deuterium in $C_6H_{12}$ led to the observation of the direct KIE ($\beta = 2.3$ at 293 °C).[7]

On the platinum catalysts, the rates of hydrogenation of benzene were identical whatever the combination of the deuteriated and light molecules, i.e. there were no KIE.[149] However, one should note that the measurements were performed at only one temperature (85 °C). Comparison of the rates of the exchange reactions in the $C_6H_6 + D_2$ and $C_6D_6 + H_2$ systems showed that the KIE is then fairly large and that $\beta$ ranges from 6.0 to 7.0 on both nickel and platinum.[149]

An example of the discrepancies between the estimates of the KIE can also be provided by the data of an investigation[100] where the disproportionation of propene on rhenium oxide was studied and of one[106] where the same reaction was carried out on a molybdenum catalyst. In the former case no KIE was observed, while in the latter the rate of reaction changed in the presence of deuterium at specific sites in the molecule. The absence of the KIE in the hydrogenolysis of n-pentane on platinum and nickel[23] conflicts with the significant isotope effect in the hydrogenolysis of various paraffins on the oriented crystal faces of platinum.[150]

The reverse KIE are not rare in hydrogenation reactions when $H_2$ is replaced by $D_2$.[147] They have been noted in the hydrogenation of acetone,[151] toluene,[10] and 2-methylfuran [152] on nickel and of 5-methylfurfural on palladium,[120] in the reaction between methane and carbon monoxide on the ruthenium,[153] nickel,[154,155] and palladium [156] catalysts, and in the synthesis of methanol on the $ZnO-Cr_2O_3$ and $Cu-ZnO-Al_2O_3$ catalysts.[157] The reverse KIE in the hydrogenation of benzene was already mentioned above. However, the manifestation of the reverse KIE in hydrogenation can be in no way regarded as a general rule. Reverse KIE have been observed, for example, in the hydrogenolysis[150] and skeletal isomerisation[23,150] of paraffins on platinum. On the other hand, the direct effects have been observed in the hydrogenation of isoprene,[13] hexene,[21] cyclopentadiene,[91] mesityl oxide,[15] and dimethylethynylmethanol [111] on various palladium catalysts, of cyclohexanone on the copper–magnesium catalyst,[19] of isoprene on the calcium–nickel phosphate catalyst,[6] and of piperylene on the NaY zeolite.[158] In all the studies quoted the occurrence of the KIE was regarded as evidence for the involvement of hydrogen in the slow stage of the reaction. On the other hand, the absence of the KIE in the hydrogenation of n-decane,[17] the dehydrogenation of cyclohexanol $C_6H_{11}OD$,[19] the hydrogenolysis of thiophen[20] and n-pentane,[23] and the disproportionation of propene[100] is regarded as proof that hydrogen is not involved in the slow stages of these processes.

The measurement of the KIE when hydrogen is replaced by deuterium in specific positions in the molecule constitutes a very effective procedure. This makes it possible not only to infer the very fact of the involvement of a bond with hydrogen in the slow stage of the reaction, but also makes it possible to determine the location of such bonds. For example, a KIE has been observed in the hydrogenation of toluene when fully deuteriated or ring-deuteriated molecules were made to react (the values of $\beta$ at 216 °C were 0.73 and 0.85 respectively), whereas the KIE was absent when hdyrogen was replaced by deuterium in the methyl group,[10] i.e. as was to be expected, the hydrogen in the methyl groups is not involved in the slow stage.

In the study of the *cis–trans* isomerisation of mixtures of *cis*-but-2-enes having the compositions $C_4H_8$ and $C_4D_8$ and also of $CH_3CDCDCH_3$ and $C_4D_8$ on aluminophosphate catalysts, an appreciable KIE was observed ($\beta \cong 2.5$).[140] On the

other hand, the coisomerisation of a mixture of *cis*-but-2-enes $C_4H_8$ and $CH_3CDCDCH_3$ took place without an isotope effect. Hence follows the conclusion that the methyl groups of but-2-ene participate in the slow stage.

Similar examples are known also for oxidation reactions. In the extensive oxidation of perdeuteriopropene and propene having the formula $CD_3CHCH_2$ on the irridium catalyst, a large isotope effect was observed following the oxidation of $CH_3CDCH_2$ and especially $CH_3CHCD_2$ molecules. $\beta \cong 1$ was obtained.[159] Consequently the slow stage of this reaction involves the dissociation of a C–H bond in the methyl group. Comparison of the rates of oxidation of the methanols $CH_3OH$, $CH_3OD$, and $CD_3OD$ to formaldehyde on molybdate catalysts also showed that here the rate-limiting stage is the abstraction of hydrogen from the methyl group.[160] The dissociation of a C–H bond also limits the rate of oxidation of butanol on platinum,[161] because a KIE was observed only in the presence of deuterium in the hydrocarbon component of the molecule but not in the hydroxy-group.

The extensive oxidation reactions of cyclohexene, acetaldehyde,[161] and formic acids[162] on platinum also occurred with a large isotope effect. On the other hand a KIE was not observed in the oxidation of acetic acid,[162] benzene,[161] and aniline.[163]

As already mentioned, the magnitude of the KIE depends on the reaction temperature: $\beta$ usually approaches unity as the temperature increases,[15,24,150] but a linear increase of the KIE has also been observed—in the reaction between methane and carbon monoxide on the nickel catalyst.[155] The temperature dependence of the KIE in the hydrogenolysis and isomerisation of saturated hydrocarbons has been studied.[150] The pressure of the reactants can also influence the magnitude of the effect.[148,150] A change in the sign of the effect, from direct to the reverse, has been observed with decrease of the ratio $H_2(D_2)$/hydrocarbon in the dehydrocyclisation of isooctane on platinum.[148,164] This emphasises yet again that it is insufficient to measure the KIE under only one set of arbitrarily selected conditions.

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To what has been said above, we may add that an important feature of many studies carried out in recent years is the use of isotope methods in combination with other procedures for the investigation of the mechanisms of catalytic reactions. This results in a mutual enrichment of their possibilities and promotes a deeper understanding of the characteristics of the reactions of organic molecules on the surfaces of catalysts. In particular, analysis of the isotope composition of the products formed when hydrogen is replaced by deuterium has been applied successfully to the study of catalysis by the thermal desorption and programmed temperature reaction methods[165–167] and also by the mass spectrometry of secondary ions.[168] The use of deuterium in the study of the mechanisms of catalytic reactions by the non-stationary response method has also proved very useful.[148]

The great interest aroused in the mechanism of catalysis will undoubtedly promote a wider adoption of isotope methods involving the use of deuterium, especially in combination with other procedures.

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# Computer Chemistry

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The state, problems, and prospects of a new branch of chemistry, computer chemistry, associated with the application of computers to the solution of chemical problems is described. The application of computers in quantum chemistry, in solution theory, in the search for new medicinal drugs, in the identification of chemical compounds from spectroscopic data, and in the development of the syntheses of new chemical compounds is examined. The level of the problems solved in the above fields of computer chemistry is demonstrated for specific examples.
The bibliography includes 64 references.

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## I. INTRODUCTION

We are now witnessing a major revolution in natural sciences associated with the wide-scale introduction of computers into all their branches, both experimental and theoretical. This process has taken place particularly vigorously during the last decade, a period during which there has been a considerable growth in the manufacture of fast computers and virtually all those investigators who are interested have gained access to powerful computers. The most important consequence of the introduction of computers into natural sciences has been the appearance of new branches of these sciences. Thus, together with experimental and theoretical physics, computer physics has appeared and in chemistry we have computer chemistry.† The time when we shall be able to speak of computer biology is apparently not distant. Whereas until recently there existed two ways of securing knowledge, either by carrying out experiments or by creating a theory, nowadays one may speak of the appearance of a third way associated with the use of computers.

The study of the physical and chemical properties of molecules, atoms, radicals, and ions in the gas, liquid, and solid phases with the aid of computers is the subject of computer chemistry. Some experience has already been gained in the solution of these problems with the aid of computers and in this review we shall characterise briefly the level of the problems solved at present by the methods of computer chemistry and we shall discuss the advances, problems, and prospects of this branch of science.

## II. QUANTUM CHEMISTRY

Computer quantum chemistry constitutes the most developed branch of computer chemistry. Quantum chemists were some of the first to initiate the use of computers in their research; as a result, quantum chemists engaged in calculations are as a rule highly qualified programers and quantum-chemical programs are some of the most complex among scientific and technical programs# together with programs for nuclear physics and programs for the calculation of the trajectories of space devices.

The need to use computers in quantum chemistry is due to the fact that, although the Schrödinger equation has been known for more than fifty years, nevertheless it has been possible to solve it analytically only for the simplest cases—the hydrogen atom and the $H_2^+$ molecular ion. Successful quantum-chemical calculations involve the use of a whole series of approximations for the solution of the Schrödinger equation. Nevertheless, even the approximate equations obtained for any complex atoms and molecules can be solved only with the aid of computers. The most logical methods in quantum chemistry are the non-empirical (or *ab initio*) methods. This term is understood to embrace a fairly wide set of approximate methods for the solution of the Schrödinger equation for atoms and molecules. It is not fortuitous that the Latin term "*ab initio*" which can be translated as "from the beginning" has found extensive applications in all languages for the designation of these computation methods, because it emphasises that the *ab initio* methods do not use any additional experimental data (ionisation potentials, atomisation energies, etc.) apart from fundamental physical constants (the velocity of light, the Planck constant, and nuclear and electronic charges and masses) and have been devised on the basis of the Schrödinger method by introducing various physically justified approximations. By the successive abandonment of such approximations, it is possible to increase the rigour and accuracy of these calculations.

The simplest version of the *ab initio* approach consists in the solution of the system of Hartree–Fock–Roothaan (HFR) equations:

$$\sum_{\nu=1}^{n} c_{i\nu}(F_{\mu\nu} - \varepsilon_i S_{\mu\nu}) = 0, \text{ where } \mu = 1 \ldots n \ . \qquad (1)$$

In this approach the wave function is used in the form of a Slater determinant and the delocalised molecular basis orbitals (MO) are expanded in terms of one-centre atomic orbitals (AO) and the self-consistent field approximation is employed:

†A series of international journals (Computers and Chemistry, Journal of Computational Chemistry, and Journal of Chemical Information and Computer Sciences), devoted to computer chemistry are already being published.

#For example, the GAUSSIAN-80 program consists of one hundred thousand FORTRAN operators.[1]

$$\Psi^{MO} = \sum_{\mu=1}^{n} c_\mu \varphi_\mu . \qquad (2)$$

At the present time there are already tens of non-empirical programs applying the HFR method. Among foreign programs, these are GAUSSIAN, HONDO, IBMOL, POLYATOM, MOLECULE, DISCO, and others while among Soviet programs mention may be made of SPUSH) Moscow State University, KVANT (Institute of General Chemistry of the USSR Academy of Sciences), and others.

It is at present difficult to estimate what are the largest molecular systems susceptible to calculations by the HFR method. Fairly accurate calculations for molecules of the type $C_6F_6$ are possible even on minicomputers of the NORD-500 type.[2] Naturally, on large computers the scope for calculations is significantly greater and calculations have already been made for the $Fe[C_5(CH_3)_5]_2$ molecule[3] containing 51 atoms and 176 electrons, a complex of the prophyrin ring with an iron atom and an ammonia molecule adsorbed on it,[4] and a cluster of 13 copper atoms.[5]

In the limiting case where the basis set of AO is complete, it is possible to obtain by this method the exact total Hartree–Fock energy of the molecule, which constitutes a fairly good approximation to the exact non-relativistic value ($\geqslant$99.9% of the exact value). However, the residual error is comparable to the energies of chemical bonds and the HFR method therefore provides a poor description of the dissociation energies of chemical bonds. The example involving the dissociation energy of the $F_2$ molecule, where the HFR method yields a negative value, is well known. Nevertheless, many molecular characteristics can be obtained with satisfactory accuracy in calculations by the HFR method. The experience gained in calculations for several hundreds of molecules, ions, and radicals has shown that in this approach the calculated equilibrium intermolecular distances as a rule differ from the experimental values by 0.02–0.05 Å, the valence angles differ by 1–3°, the force constants differ by 10–15%, the vibration frequencies differ by 5–10%, the energies of isodesmic reactions, in which the number of bonds is kept constant (for example, HCCH + $H_2$ → $H_2CCH_2$), differ by 5–10 kcal mol$^{-1}$, the barriers to intramolecular rearrangements differ by 2–5 kcal mol$^{-1}$, the valence ionisation potentials differ by 1–2 eV, and the dipole moments differ by 0.2–0.5 D.[6–8] These data show that the HFR method is entirely suitable for semi-quantitative estimations of many molecular characteristics. Although the cost of calculations by the HFR method is still high, nevertheless, bearing in mind that the calculations yield a large number of molecular characteristics which are not accessible simultaneously to any one experimental method, such calculations may be justified economically.

The second group of computational *ab initio* methods, which have developed particularly vigorously during the last five years, makes it possible in principle to obtain a virtually exact solution of the non-relativistic Schrödinger equation. In these methods account is taken of the correlation energy of the electrons, which is equal to the difference between the Hartree–Fock energy and the exact non-relativistic adiabatic energy of the molecule. A large set of such methods, both methods adapted for the solution of specific problems such as the calculation of ionisation potentials and electron affinities (the method of Green functions, the method of equations of motion, etc.) and more general computational methods for the calculation of the total energy and the wave function (the method of configuration interaction, the multiconfiguration self-consistent field method, and perturbation theory), have now been developed.

The configuration interaction (CI) method is most frequently used to take into account the electron correlation energy in *ab initio* calculations.[9–11] In it the total wave function is formulated as a linear combination of Slater determinants corresponding to different electronic configurations:

$$\Psi_{tot} = \sum_{k=1}^{M} a_{kl}\varphi_k , \qquad (3)$$

where $M$ is the number of configurations taken into account. The calculation reduces to the computer solution of the following system of equations:

$$\Sigma a_{kl}(H_{kl} - E_l\delta_{kl}) = 0 . \qquad (4)$$

In calculations by the CI method several approaches are used for the selection of the configurations to be taken into account. One of the approaches, involving a limited CI expansion (3), is based on the estimation of the coefficients $a_{kl}$ in terms of perturbation theory. Only the determinants whose coefficients $a_{kl}$ are greater than a certain quantity are then left in expansion (3). In this approach it is possible to select the most significant configurations and, using not unduly long expansions, account can be taken of most of the electronic correlation energy.[11] Another approach, in which account is taken of the complete set of configurations of any type, for example singly and doubly excited configurations (CI-SD) or only doubly excited configurations (CI-D), is also widely used.[12] This method of taking into account the correlation energy uses the fact that electrons are mainly correlated in pairs. Indeed, in CI-SD and CI-D calculations it is possible to include 85–95% of the valence correlation. Many programs using this CI method are now available; the first approach is employed, for example, in the SPUSH (Moscow State University) program and the second in the GAUSSIAN-80 program.

Another widely used method whereby the electron correlation energy is taken into account is that of perturbation theory (PT).[12–14] This approach is based on seeking the solution of the exact Schrödinger equation:

$$H\Psi = E\Psi$$

on the basis of the known solutions of the Schrödinger equation

$$H^{(0)}\varphi^{(0)} = E^{(0)}\varphi^{(6)}$$

with a model Hamiltonian $H^{(0)}$ which differs from the exact equation by a small perturbation $W$. The wave function $\Psi$ and the energy $E$ are sought in the form of the series

$$\Psi = \varphi^{(0)} + \varphi^{(1)} + \varphi^{(2)} + \ldots$$
$$E = E^{(0)} + E^{(1)} + E^{(2)} + \ldots .$$

In quantum-chemical calculations the Hartree–Fock–Roothaan Hamiltonian is chosen as $H^{(0)}$ and the perturbation $W$ is the operator describing the electronic correlation:

$$W = \sum_{i>j} \frac{1}{r_{ij}} - \sum_{i>j} (2J_{ij} - K_{ij}) .$$

For this choice of $H^{(0)}$ and $W$, $E^{(1)}$, i.e. the first correction to the electronic energy of the molecule, vanishes and the first non-zero contribution comes from the second-order perturbation theory (the energy $E^{(2)}$).

The contributions to the energy by each order of the perturbation theory can be formulated by means of a diagrammatic representation, which has proved extremely useful for the construction of algorithms for the corresponding program. Because of this, programs taking into account fully four PT orders were devised immediately in several laboratories in the world. One such program is the POLYCOR program developed at the Bratislava university (Czechoslovakia); the Gaussian-82 program, developed at the Carnegie-Melon university (USA), also includes the corresponding set of subprograms. It is of interest to discover how rapidly the

members of the PT series diminish. Table 1 presents the corrections to the total energies of the $LiBH_4$ and $Li_2BeH_4$ molecules arising from the second-, third-, and fourth-order perturbation theories. We may note that a slow decrease of the members of the PT series might have been expected for these molecules owing to the quasidegeneracy of the 2*s* and 2*p* shells of the Be and B atoms. Nevertheless, Table 1 shows that successive members of the PT series decrease rapidly. For the $LiBH_4$ and $Li_2BeH_4$ molecules, the contribution by the second-order perturbation theory is 90–95% of the valence correlation energy and calculations for the HF, $H_2O$, and BH molecules have shown[16,17] that the sum of the contributions by the second-, third-, and fourth-order perturbation theories takes into account 98–99% of the valence correlation energy. It must be emphasised that, for molecules having low-lying excited states, the PT series can diverge, as happens, for example, for the $C_4$ molecule.[18]

**Table 1.** The contributions to the total energies of the $LiBH_4$ and $Li_2BeH_4$ molecules by different orders of perturbation theory.[15]*

| Molecule | $E^{HFR}$, a.u. | $E^{(2)}$, a.u. | $E^{(3)}$, a.u. | $E^{(4)}$, a.u. |
|---|---|---|---|---|
| $LiBH_4$ | −34.4535 | −0.1379 | −0.0211 | −0.0068 |
| $Li_2BeH_4$ | −31.8522 | −0.0787 | −0.0178 | −0.0063 |

*DE + P + D basis set.

Since we are unable to consider other methods for taking into account the electronic correlation energy, we shall deal briefly with the new possibilities provided by *ab initio* methods with allowance for electronic correlation in quantitative calculations of molecular characteristics.

*Ionisation potentials.* The results of the calculations of ionisation potentials (IP) by the method of Green functions have been summarised[19] and it has been concluded that the maximum error in the calculated IP is between 0.1 and 0.25 eV depending on the basis set used in the calculations. Table 2 presents the calculated experimental IP of the ethylene molecule as a typical example.

**Table 2.** Calculated* and experimental ionisation potentials (eV) of the ethylene molecule.[20]

| Symmetry of MO | Calcn. | Expt. |
|---|---|---|
| $1b_{2u}$ | 10.44 | 10.51 |
| $1b_{2g}$ | 13.04 | 12.85 |
| $2a_g$ | 14.70 | 14.66 |
| $1b_{3u}$ | 16.07 | 15.87 |
| $1b_{1u}$ | 19.44 | 19.23 |

*The time required to calculate one ionisation potential by the method of Green functions on the IBM 360/91 computer is only 4–5 min.

*Electronic transition energies.* Either the standard CI method or the CI method based on several initial configurations (CI-SIC) are most often used to calculate the electronic transition energies. As for the ionisation potentials, here the error in the determination of the energies of vertical electronic transitions does not exceed 0.1–0.2 eV and is in fact within the limits of the error of their experimental determination. As an example, Table 3 presents the calculated electronic transition energies for the *trans*-butadiene molecule.

**Table 3.** The energies of the electronic transitions (eV) in the *trans*-butadiene molecule.[21]

| Symmetry of state | Calcn.* | Expt. |
|---|---|---|
| $^3B_u$ | 3.31 | 3.2; 3.22; 3.3 |
| $^3A_g$ | 4.92 | 4.93; 4.9; 4.8 |
| $^1B_g$ | 6.20 | 6.22 |
| $^1A_u$ | 6.53 | } 6.567 series |
| $^1B_u$ | 6.67 | |
| $2^1A_u$ | 6.72 | |
| $2^1A_g$ | 7.02 | 7.06 |
| $2^1B_g$ | 7.29 | 7.328 |
| $3^1A_g$ | 7.53 | 7.481 |

*Calculation by the CI method taking into account all the valence-excited configurations.

*Dissociation energies.* It is known that the determination of the dissociation energies of molecules to within the experimental accuracy presents the greatest difficulty for *ab initio* calculations. Table 4 lists the dissociation energies of certain molecules for which the HFR method introduces large errors; however, it is seen that allowance for the correlation energy within the framework of perturbation theory diminishes the errors in the calculated dissociation energies of these molecules to approximately 5 kcal $mol^{-1}$. These results show that, for small moelcules and especially for radicals, ions, and other chemically active species, whose experimental study involves considerable difficulties, computer calculation can constitute an alternative approach to the determination of their dissociation energies.

**Table 4.** The calculated and experimental dissociation energies (kcal $mol^{-1}$) of the $H_2$, $N_2$, and $NH_3$ molecules.[22]

| Method* | $H_2 \rightarrow 2H$ | $N_2 \rightarrow 2N$ | $NH_3 \rightarrow N + 3H$ |
|---|---|---|---|
| HFR | 83.7 | 114.8 | 200.8 |
| HFR + PT(2) | 103.7 | 231.2 | 290.5 |
| HFR + PT(2-3) | 107.2 | 207.7 | 288.1 |
| HFR + PT(2-4) | 108.1 | 223.6 | 292.4 |
| Experiment | 109.4 | 228.4 | 297.3 |

*PT(2), PT(2–3), and PT(2–4) are corrections to the correlation energy calculated within the framework of second-, second- and third-, and second, third-, and fourth-order perturbation theory respectively.

*Vibration frequencies.* At the present level of the accuracy of the calculations of vibration frequencies, one may hope to achieve results with an error of 1–2%. Table 5 lists the fundamental frequencies of the water molecule calculated by the CI method for several configurations.

Table 5. The calculated and experimental fundamental vibration frequencies ($cm^{-1}$)* of the $H_2O$ molecule.[23]

| Method of determination | $\nu_2$ | $\nu_1$ | $\nu_3$ |
|---|---|---|---|
| MC-CISD* | 1623 | 3667 | 3752 |
| Experiment | 1595 | 3657 | 3756 |

*The method of configuration interaction based on an initial multiconfiguration function.

*Equilibrium geometrical parameters.* Allowance for the correlation energy makes it possible to increase the accuracy of the determination of the calculated geometrical parameters to within 0.01 Å for internuclear distances and 0.1° for valence angles. Such accuracy in the above quantities is comparable or even greater than the accuracy of their determination for molecules, radicals, and ions with more than two atoms.

The high accuracy of the *ab initio* calculations of many molecular characteristics has made them a powerful instrument, independent of experiment, for the investigation of molecules and the application of these methods has significantly expanded our ideas. We shall quote only two examples. In chemistry one of the firmly established postulates is that the maximum valence of carbon is four and, in relation to univalent ligands, its maximum coordination number is therefore also four. However, in 1982–1983, Schleyer and co-workers[24,25] predicted by means of *ab initio* calculations the existence of the stable molecules $CLi_5$ and $CLi_6$. In their equilibrium configurations these molecules have the structure of a regular trigonal bipyramid and an octahedron respectively. In addition, on the basis of non-empirical calculations, Schleyer and co-workers concluded that the hyperlithium molecules $NLi_5$, $OLi_5$, $NLi_4$, $OLi_4$, $FLi_4$, $OLi_3$, $FLi_3$, and $FLi_2$ and also the hypersodium molecules $ONa_3$, and $ONa_4$ are stable with respect to unimolecular dissociation.[24–26] The existence of some of these molecules has been confirmed experimentally. Thus the $CLi_5$ molecule has been detected mass-spectrometrically in the interaction of $CCl_4$ with lithium atoms in the gas phase. When lithium atoms diffused through a graphite membrane, $CLi_6$ and $CLi_5$ were also detected mass-spectrometrically. Mass-spectrometric measurements also led to the detection of $OLi_5$, $OLi_4$, $ONa_3$, and $ONa_4$ (for further details, see Schleyer[25]). The theoretically predicted discovery of this new class of hyperlithium and hypersodium molecules has extended our ideas concerning the possible valence states and coordination numbers of atoms and molecules.

Non-empirical calculations of the potential surfaces for a large number of structurally non-rigid molecules showed that our ideas about molecular structure are limited. The point is that modern ideas about molecular structure constitute a complex conglomerate of quantum and classical concepts. Whereas the concept of wave functions has been rapidly introduced into chemistry for the description of the electronic subsystem of the molecule as the foundation of quantum mechanics, for the nuclear subsystem the classical description has to a large extent persisted to this day. There are objective reasons for this: in the first place these are the much greater mass of the nuclei and the shape of the potential surfaces (PS) for many molecules, where a deep minimum in the PS corresponds to the equilibrium configuration (in this case one minimum on the PS is sufficient for the description of the molecular structure). For the lowest vibrational levels of such molecules, a quasi-rigid rotator–harmonic oscillator model is satisfactory. This molecular model makes it possible to retain all the classical ideas concerning the length, energy, and force constant of the chemical bond and the subdivision of all interactions into valence and non-valence types. For quasi-rigid molecules, the vibration amplitudes of the nuclei are small compared with the chemical bond lengths and the transition from the classical sphere-rod or sphere-spring model to the quantum model by the introduction of nuclear density functions does not lead to any significant modification of the classical ideas.

Nevertheless it is clear that the quantum nature of nuclei must be manifested in the molecular structure and for many problems it is essential to resort to the nuclear density functions. One can indicate several fields where the introduction of the concept of nuclear density functions is necessary for the description of the structure. In the first place these are highly excited vibrational states and "activated" or "transition" complexes in reactions. Finally, there exists a large class of molecules for which the approach restricted to one minimum in the PS is insufficient even for the lowest vibrational levels. These are the so-called structurally non-rigid or polytopic molecules on the PS of which there are at least several minima having similar energies and separated by low barriers. Such molecules have been known since the 1930s; they include organic molecules in which there is a possibility of hindered rotations about single bonds, amines in which inversion takes place, pentacoordinate $MX_5$ molecules with pseudorotation, etc. However, in these molecules "movements" with a large amplitude occur between atoms which are not linked by valence bonds and the classical subdivision of interactions into valence and non-valence types is not therefore infringed.

Non-empirical calculations of the PS for tens of molecules have shown[27] that large-amplitude movements (of the order of the chemical bond length) of molecules are possible also for atoms which are linked by valence bonds from the classical standpoint. The movements of the $Li^+$, $Na^+$, and $K^+$ cations around the $CN^-$, $BH_4^-$, and $BF_4^-$ anions,[28–33] rearrangements with intramolecular decomposition of anions in the salts $Li_2BeH_4$ and $Li_2BeF_4$,[34,35] and the intramolecular movement of the $H^+$ cations along the carbon skeletons of carbonium ions[36] and of $H^-$ anions along the beryllium and boron skeletons of hydroberyllates and hydroborates[37] may be quoted as examples. In order to describe such molecules, it is necessary to consider large regions of PS along "non-rigid" coordinates. In the vibrational adsorption spectra the lines are split owing to tunnelling through low barriers[38] and the vibrational states of these molecules must be classified in terms of irreducible representations of either the complete transposition-inversion groups or their subgroups. Curves describing the temperature variation of the thermodynamic functions of structurally non-rigid molecules show inflections and the rigid rotator–harmonic oscillator must not be used to calculate the thermodynamic functions. However, the presence of a number of maxima in the nuclear density function greater than the number of atoms in the molecule, which cannot be described within the framework of classical ideas, must be recognised as the most unusual manifestation of the structural non-rigidity of molecules.

The examples presented show that computer quantum chemistry provides an alternative approach to the study of molecules and makes it possible to discover new classes of molecules, to achieve a deeper understanding of molecular structure, and to obtain numerical values of molecular characteristics.

## III. MODELLING OF SOLUTIONS

As mentioned above, the quantum chemistry of gas-phase molecules has already in fact reached the level of computer experiments. However, the majority of chemical reactions take place in solution and allowance for solvation effects constitutes an extremely difficult problem and again new significan progress has been achieved as a result of the employment of computers.

Several approaches have been developed in solution theory. In the most logical approach, the calculation is carried out by one of the quantum-chemical methods described in the previous section for a solute molecule surrounded by the maximum possible number of solvent molecules. This approach is referred to as supermolecular,[39] but it is evident that its realisation involves considerable computational difficulties, although for comparatively simple molecules such calculations have in fact been carried out.

Approximate methods are used in the study of solutions of complex organic and biological molecules: the direct optimisation method,[40] the molecular dynamics method,[41,42] the Monte Carlo method,[43,44] and others. Owing to the small amount of space available in this review, we shall confine ourselves to the consideration of the description of the structure and thermodynamics of solutions by the Monte Carlo method, which has come to be widely employed in recent years. The Monte Carlo (MC) technique is a procedure for the estimation of multiple integrals with the aid of random numbers. The average energy of a liquid system, obtained by averaging the energy values over a canonical *ensemble*, is a multiple integral of this kind. The kinetic energy is known and, for the determination of the potential energy $v(q_1 \ldots q_n)$, it is necessary to calculate its average value:

$$\langle v \rangle = \int v(q_1 \ldots q_n)\, p(q_1 \ldots q_n)\, dq_1 \ldots dq_n \quad , \qquad (5)$$

where

$$p(q_1 \ldots q_n) = \frac{\exp[-v(q_1 \ldots q_n)/kT]}{\int \exp[-v(q_1 \ldots q_n)/kT]\, dq_1 \ldots dq_n} \quad . \qquad (6)$$

The potential of the interaction between $n$ molecules can be represented as follows:

$$V = \sum v(ij) + \sum v(ijk) + \ldots \sum v(ij \ldots n) \quad . \qquad (7)$$

In real calculations only the first sum is left in expansion (7).

The parameters of the pair potential can be determined either by *ab initio* calculations or from experimental data. The first procedure is more effective because *ab initio* calculations make it possible to investigate the interactions of molecules for any orientations, whereas experimental information refers to the equilibrium configurations. Clementi[39] examined 50 classes of atoms (H, C, O, N, and certain other atoms most frequently encountered in organic and biological molecules) as a function of the valence state of the given atom and of its environment. For these classes of atoms, he determined the parameters of the atom–atom potentials from his *ab initio* calculations; these parameters are most frequently used in calculations by the MC method.

The study of the structure and thermodynamics of solutions by the MC method reduces to the random generation of the configurations of the solvent molecules around the solute molecule, which is placed at the origin of coordinates. In order to obtain statistically reliable information, it is necessary to sort through $10^9$ configurations, many of which are energetically unfavourable and therefore very improbable. In order to exclude such configurations, one employs the Markov chain technique which selects configurations taking into account the Gibbs distribution. Evidently, the larger the number of solvent molecules considered, the more reliable is the information which can be obtained concerning solvation effects. In the calculations carried out a present, account is taken as a rule of between 100 and 500 water molecules.

One of the first systems investigated by the *ab initio* MC method, was water.[45] These calculations showed that the radial distribution function for the oxygen atoms in water calculated *ab initio* without using empirical data agrees well with the experimental curve (Fig. 1). The average energy of the interaction of the molecule with the remaining molecules is approximately 7 kcal $mol^{-1}$ according to the calculations by the MC method. Apart from pure water, aqueous solutions of LiF,[46,47] and glycine, certain other aminoacids, and other biologically important molecules[39] were investigated. The MC method was applied even in the study of the hydration of the complex DNA molecule; in these calculations a fragment of the DNA double helix was placed in a hydration shell made up of 477 water molecules.[39]

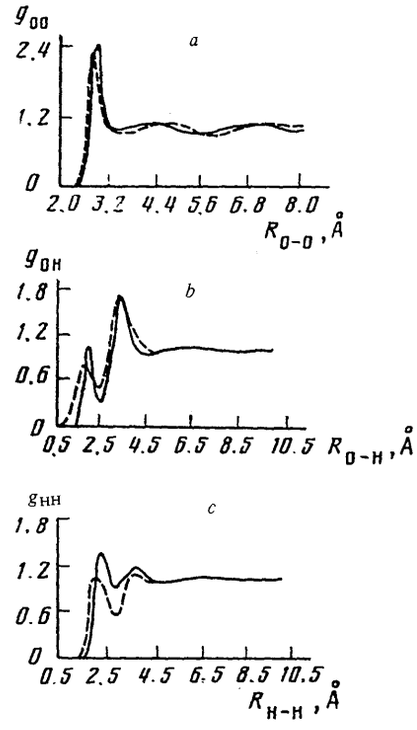



**Figure 1.** Comparison of the experimental (continuous lines) and calculated by the *ab initio* method (dashed lines) radial distribution functions: a) $g_{OO}$; b) $g_{OH}$; c) $g_{HH}$.[45]

The influence of solvation on the tautomerism of 4-hydroxypyridine and 4-pyridone has been investigated within the framework of the MC method.[48] In these calculations, the Clementi potentials were used and account was taken of 110 water molecules; it was found that the solvation energy of

4-pyridone is greater by ~5 kcal $mol^{-1}$ than that of 4-hydroxypyridine, which agrees with the experimental value (~5 kcal $mol^{-1}$). Naturally, one must not overestimate such good agreement between the calculated and experimental quantities because 110 water molecules is not a very large number for a reliable modelling of the solvation of these molecules. We may note that the MC method permits the investigation of the influence of temperature on the structure and thermodynamics of solutions.[44]

A very interesting aspect of solution theory involves the combination of the supermolecular and Monte Carlo methods, in which the geometrical structure of the solvation shell is determined by the MC method, while a quantum-chemical calculation makes it possible to determine the influence of solvation on the electronic structure of the solute molecule, which influences in its turn the electronic structure of the solvent molecules.

## IV. MOLECULAR DESIGN OF MEDICINAL DRUGS

The major advances in medicine achieved during the last decade are to a large extent due to new highly effective medicinal drugs. However, in order to introduce new drugs into medical practice, it is necessary to synthesise and test the physiological activities of approximately 20000 chemical compounds, which requires up to 7–10 years of work by investigators and a large financial outlay. The use of the computer-aided molecular design of new chemical compounds makes it possible to overcome these difficulties and leads to great possibilities in the purposeful search for medicinal preparations.

The essential feature of the new approach is that the physiological action of a medicinal drug is related to its stereospecific interaction with a receptor, which can be hydrophobic or of the type involving hydrogen bonding between the active fragment of the drug molecule (pharmacophor) and the biologically important centre of the receptor. At the molecular level, the problem therefore reduces to isolating the active and toxic fragments of the drug molecule and to the determination (by considering both the short-range and long-range environment) of the optimum chemical composition and structure of the molecule such that the useful interaction between the pharmacophor and the receptor is most favourable, while toxic fragments are as far as possible absent. The isolation of such active and toxic fragments can be achieved by comparing the useful biological activities and toxicities of a large number of compounds in which individual fragments are substituted in succession.

After this stage of the research has been carried out, the problem of increasing the physiological activity and of decreasing the toxicity of the preparation can be solved in several ways. The most logical procedure involves a direct non-empirical quantum-chemical calculation of the electronic structures of a set of different derivatives of the initial molecule with the receptor model. The results of such calculations can be compared with, for example, the strength of the hydrogen bond between the active centre of the preparation and the receptor, which might serve as a basis for the selection of molecules with the highest physiological activity. However, such an approach nevertheless requires much computational effort in the case of complex biologically important molecules and therefore so far other simpler procedures are used.

The structure of the receptor for biologically active compounds of a given series as well as the mechanism of their interaction are usually unknown *a priori* and must be determined together with the identification of the pharmacophor molecule and the determination of its optimum steric and electronic structures. An essential condition for the solution of this problem is the availability of extensive experimental data reflecting the relation between the structures and biological activities of the chemical compounds investigated. The molecules of biologically active substances are conformationally labile and an important feature of such investigations must therefore be the determination of biologically active conformations in which there is a possibility of interaction with the receptor. The selection of the total number of low-energy conformations of each molecule investigated can be carried out both by semiempirical quantum-chemical methods and on the basis of model force fields, whose parameters are determined either empirically or from non-empirical calculations for simple molecules. In the field under consideration, the method of atom–atom potentials, which makes it possible at present to investigate fairly complex molecules (for example, those of oligopeptides), has come to be most widely used among the theoretical methods of conformational analysis.

Biologically important molecular conformations contain information about the topography of the receptor and can therefore be used in the purposeful search for new compounds with a high affinity for the receptor. Apart from the steric structure of the pharmacophor, one can therefore optimise also its electronic structure.

One of such methods reduces to the calculation of the electrostatic potential surface of an isolated molecule on the assumption that the electrostatic potential reflects the ability of the active centre of the therapeutic model to form a hydrogen bond. This approach requires a preliminary quantum-chemical calculation, which, however, is carried out only for an isolated molecule. Programs for the electrostatic potential have now been developed and are included in the sets of programs for both non-empirical and semiempirical (of the CNDO, MINDO/3, MINDO, etc.) methods of calculation.

Thus the problem of the analysis of the biological activity of the drug molecule reduces to the determination of the most stable molecular conformation in which the atoms in the active centre are accessible to interaction and the environment is complementary with respect to the corresponding receptor atoms. The relevant programs have been developed and are already widely used for the solution of specific problems. We shall quote below several examples of the successful purposeful search for medicinal drugs with the aid of the methods described above.

One of the known examples is provided by a series of theoretical studies which led to a preparation analogous to somatostatin in its physiological activity but remaining active for a longer period. We may recall that somatostatin increases the susceptibility to insulin in patients suffering from diabetes, but natural somatostatin molecules retain their physiological activity in the human body for only a short time. A group of investigators led by Weber[49] analysed a series of somatostatin conformations by the molecular modelling method and identified the active component of the molecule with the aid of computer graphics. Next, nine aminoacids were removed from somatostatin in a computer experiment and it was thus possible to stabilise the structure, which was in Weber's view most complementary to the corresponding receptor atoms. When the molecule for which the calculations had been made was synthesised in the laboratory and its effect on animals was tested, it was found that the new preparation retained its activity in the animal organism 40 times longer, whilst retaining the physiological activity of the natural hormone.

Another example involves the theoretical study of cardiac glucosides used in medicine to treat heart failure. In therapeutic doses the glucosides increase the strength of the contractions of the myocardium, reduce the frequency of the

contractions of the heart, and diminish the excitability of the myocardium. A major disadvantage of the cardiac glucosides employed hitherto is their high toxicity, to the overcoming of which investigators have devoted much effort. A complete theoretical conformational analysis of 46 cardiosteroids with known biological activity and a wide variety of monosaccharide residues in the corresponding monoglycosides has been carried[50,51] by the method of atom–atom potential functions. These calculations led to the determination of the biologically active conformations of the cardiac glycosides, which made it possible to understand the steric structure of the digitalis receptor and the mechanism of the glycoside–receptor interaction and also it permitted the prediction of a series of configurations of drug molecules which should exhibit an enhanced affinity for the receptor. These studies may serve as a basis for the purposeful synthesis of new highly effective preparations.

The advances achieved by means of computer molecular design in the development of new effective medicinal drugs give rise to the hope that the use of computers will contribute also to the development of antitumour preparations.

## V. "ARTIFICIAL CHEMICAL INTELLECT"

As computers came to be used on an increasingly wide scale, it became understood that the computer can compete with man even in fields which have been traditionally regarded as intellectual. It is possible to identify two fields in chemistry where one can already speak in a certain sense of the creation of an "artificial chemical intellect". Firstly, these are problems associated with the recognition of the structure of a molecule from the available experimental spectroscopic data. Secondly, these are problems concerning the development of a strategy for the synthesis of complex organic molecules.

The development of chemistry and especially the application of physical methods to the study of molecular structure has led to an information explosion during the last decades. It is frequently much simpler to synthesise a compound than to identify it. One of the ways of solving the complex problem of the identification of a new compound consists in the recognition of a chemical compound by comparing its spectrum with one available in the literature. However, since information about the spectra of more than 100000 organic and inorganic compounds has already accumulated in the world and the amount of this information is increasing, it follows that realistically such a comparison can be made effectively only with the aid of a computer. Such computer recognition systems for chemical compounds have already been developed by Koptyug and co-workers and have been used for a number of years in the Siberian Division of the USSR Academy of Sciences.[52,53]

In another approach to the identification of compounds from spectra, the molecule is represented as a set of separate structural fragments such as aromatic rings, methyl groups, amino-groups, etc. which have characteristic spectral features. In each specific spectrum of the compound to be identified one isolates features which are regarded as characteristic. After such characteristic spectral features have been found, each is brought into correspondence with a set of competing structural fragments. Next, for any permissible set of fragments, all the possible molecular structures satisfying the overall formula and the requirements of the classical theory of valence are constructed. Among all the structures thus found, a further selection is now made on the basis of spectroscopic parameters, which are calculated, for example, in the case of infrared spectra, from the force constants of the fragments. Information about the experimental spectroscopic parameters of the fragments is stored in the computer—in a library of standard fragments. The closeness of the calculated spectrum of a particular structure to the experimental spectrum of the molecule to be identified provides the basis for a conclusion concerning the correctness of the recognition of its structure. Evidently, when several spectroscopic methods, such as mass spectrometry and infrared, Raman, NMR, and ultraviolet spectroscopy are used in the identification process, the reliability of the determination of the molecular structure increases significantly. Sets of programs for carrying out such computer analysis have been developed under Gribov's supervision[54,55] and have already been used successfully for several years.

Apart from the problem of the recognition of molecules from the spectra, computers are being introduced into another field of "chemical thinking", namely the development of a strategy in synthesis. So far several trends have been established in the computer synthesis of organic compounds.

One of them is based on the determination of the possible ways of synthesising the required compound on the basis of thoroughly investigated organic reactions. The corresponding programs have been developed in several laboratories. One of the most popular programs, LHASA, was developed at Harvard University.[56] It consists of approximately 50000 FORTRAN operators and its data bank contains information about approximately 1000 reactions. In developing a strategy for synthesis, the LHASA program as it were solves the converse problem, i.e. it begins with the molecule which is to be synthesised and then, by "breaking" the bonds in it via a series of reactions, it arrives at comparatively simple initial compounds which are either commercially available or can be readily obtained in the laboratory.

Another trend involves a formal logical approach based on the classical theory of valence, which regards a reaction as an intermolecular or intramolecular redistribution of bonds (cyclic electron transfer). In this case the ways of obtaining a given compound can be determined from its structure by the methods of graph theory and the combinatorial theory (for further details, see Zefirov and co-workers[57,58]). The advantage of this approach consists in the fact that it makes it possible to generate on a computer processes which have no direct analogues among the known reactions. The program FLAMINGO has been developed on this unique logical basis under Zefirov's supervision and has been designed to find all possible single-state processes with cyclic electron transfer in both closed and open systems taking into account specified conditons.

The application of this program to the computer synthesis of tricyclo[2.1.0.$0^{2,5}$]pentane has been described.[58] All single-stage many-centre reactions with cyclic electron transfer directed towards the synthesis of this compound were found with the aid of a computer. The following initial data were specified: (1) the graph representing the skeleton of tricyclo[2.1.0.$0^{2,5}$]pentane with numbered atoms (Fig.2); (2) information about the molecular symmetry; (3) information necessary to select the possible reactions. The computer sorted through all the possible processes involving the redistribution of bonds between the carbon atoms on the basis of the initial graph and predicted 6 three-centre, 12 four-centre, and 11 five-centre reactions with cyclic electron transfer. On the basis of special criteria, 19 reactions were then rejected and the remaining 10 (Fig.2) were recommended as possible ways of synthesising tricyclo[2.1.0.$0^{2,5}$]pentane. Some of them have not so far been applied; we may note that, since the publication of the above communication, a reaction prediced by the computer has already been carried out under laboratory conditions.[58]

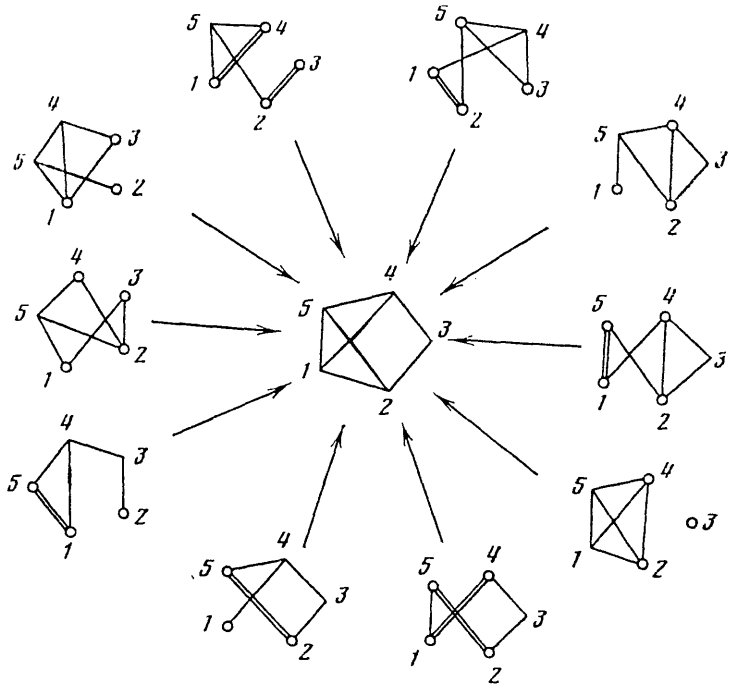
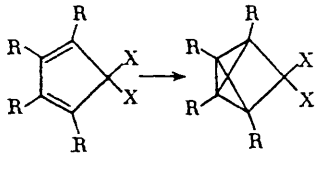


**Figure 2.** Schematic representation of the possible ways of constructing the tricyclo[2.1.0.$0^{2,5}$]pentane system found with the aid of a computer.



The field in which the "artificial chemical intellect" is developing is nowadays undergoing a vigorous growth and industrial firms interested in this problem already participate in the creation of similar programs. The computer programs described in this Section apparently simulate the thinking process of a research chemist, which in fact makes it possible to classify the operation of such programs as "artificial chemical thinking". An advantage of the computer over the human brain is that it can memorise an enormous amount of information and can manipulate it fairly rapidly.

## VI. PROSPECTS FOR THE DEVELOPMENT OF COMPUTER CHEMISTRY

Within the framework of a single review, it is at present already difficult to deal even briefly with all the fields of the rapidly developing new science—computer chemistry, which has arisen at the junction of chemistry, physics, mathematics, and computer technology. For example, apart from the applications considered above, one can point out also other important applications of computer chemistry such as the solution of the problem of optimising chemical technology with the aid of a computer and the solution of dynamic problems in the theory of elementary chemical processes. Evidently, as computers become more available to chemists, new fields of computer chemistry will arise.

The development of computer chemistry is in many respects determined by the advances in computer technology, which have been very great during recent years. Supercomputers capable of performing 100–200 million operations per second exist and, towards the end of the 1990s, the creation of supercomputers capable of 1–10 billion operations per second are expected. At the same time the size of both the operating memory of computers and the capacity of peripheral storage devices has been increasing. Discs with a capacity of one gigabyte have already been created and work on the creation of videodiscs is being completed.

The use of these new possibilities makes it possible to solve fundamentally new problems in computer chemistry, to raise the level of accuracy in the problems already dealt with, and to extend the range of applications. In quantum chemistry this involves taking into account the relativistic effects in molecules and calculations for large systems taking into account electron correlation; in principle, one may expect the appearance of dialogue programs, which would enable the chemist, before synthesising any one compound, to investigate theoretically its energy stability and the properties of its molecules. In solution theory, the supermolecular approach will become available for large organic molecules as the computer technology is improved and in methods of the Monte Carlo type it will be possible to take into account tens of thousands of solvent molecules, which will permit the investigation of bimolecular reactions in solution. In studies on molecular design, it will be possible to consider a large number of medicinal drug molecules and to take into account tens of their parameters in identifying the active centres, which will significantly increase the reliability of the prediction of the activities of new preparations. In studies on the "artificial chemical intellect", the data banks

will increase to tens of thousands of reactions, which will enable us to increase fundamentally the effectiveness of the synthetic procedures being developed; in problems on molecular structure recognition, the increase in the number of spectra in the data bank will also raise the reliability of the identification of new compounds. The development of chemistry is nowadays no longer imaginable without computers.

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During the preparation of the review for the press, a number of other review articles, devoted to various branches of computer chemistry were published.[59-64] Clementi[59] described new results obtained in the *ab initio* modelling of water (three- and four-particle interactions, and also corrections associated with zero-point vibrations were taken into account), the hydration of a DNA fragment (30 pairs of bases surrounded by 1500 water molecules), and the transport of $Na^+$ and $K^+$ ions through membrane channels. The results of the application of supercomputers to the calculation of the structure of the solvated electron and the structures of liquid sulphur, amorphous nickel, and silicon in crystalline, liquid, and low-temperature amorphous states have been discussed in a review.[60] Other communications[61-64] have been devoted to the prospects for the creation and use of supercomputers in chemistry, the computational aspects of the determination of crystal structures, and non-empirical quantum-chemical methods.

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# Experimental Study of Chemical Processes under Dynamic Compression Conditions

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The results are given of studies on the creation of a set of systems for the preservation of specimens of condensed substances subjected to dynamic pressures with different types of stress applied to the specimens: with single and stepwise shock compression and also with nearly isentropic compression. The conditions in the compression of substances in protective tubes using cylindrical and planar compression schemes are examined. Examples of various chemical processes under these conditions are given, attention being concentrated on the reactions of organic substances.
The bibliography includes 90 references.

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## I. INTRODUCTION

New methods for the generation of high pressures in a condensed medium, based on the use of powerful shock waves (SW), have been proposed and developed in recent years. In particular, shock waves have been generated in the test substance by the action of detonation waves from a chemical explosive on a specimen in contact with the explosive charge or as a result of impact by bodies accelerated to high velocities by the detonation products of the explosive. In condensed (solid or liquid) explosives, up to $8\times10^6$ kJ $m^{-3}$ of chemical energy can be concentrated per unit volume; the energy is liberated under detonation conditions, i.e. in the course of the ultrasonic propagation of the front of an exothermic chemical reaction in the explosive. After the sharp increase of pressure at the shock wave front, the pressure diminishes owing to the chemical process in the reaction zone. At the end of the reaction zone the detonation products expand and are accelerated in the direction of propagation of the reaction zone. The mixture of gaseous products at the end of the reaction zone has a density of up to 2.5 g $cm^{-3}$. The detonation wave propagates at a constant velocity, so that the energy losses by the SW are continuously made good by the energy liberated as a result of the chemical reaction in new portions of the explosive.

The detonation wave excited SW in the adjoining medium whose intensity depends on the power of the explosive and the dynamic rigidity of the medium $\rho_0 D$, where $\rho_0$ is the initial density of the material of the specimen and $D$ the velocity of the SW front. For example, in the detonation of an explosive at a rate of $\sim8\times10^3$ m $s^{-1}$, pressures of ~45 GPa develop in a steel bar in contact with the charge. Experiment shows that, when a steel plate is accelerated by the detonation of the same explosive, its impact against steel can generate pressures in the specimen which are three times as great.

The behaviour of gases and condensed substances on compression by means of SW shows significant differences. When SW are propagated in a gas, even low pressures induce a marked compression and a considerable increase of temperature by virtue of the high compressibility of the gas. The pressure in the gas has a thermal origin and is always proportional to the temperature. At high temperatures various physicochemical processes occur in gases: excitation of molecular vibrations, dissociation, ionisation, and chemical reactions.

On compression by SW, a condensed substance behaves differently, because the repulsive forces between atoms must be overcome in order to increase density. For this reason, an internal pressure of non-thermal character arises on shock compression in addition to the "thermal" pressure. With increased compression, the first component of the pressure associated with the thermal movement of atoms increases; this leads to limiting degrees of compression. This does not occur under isentropic or isothermal compressions, where an increase of pressure always entails an increase of density.

The first studies showed that the use of shock compression is productive in the study of dynamic compressibility (shock adiabats) of metals, the determination of null isotherms, and the derivation of semi-empirical equations of state in the range of pressures up to several hundreds of GPa and temperatures of $\sim10^4$ K.[1,2] We may note that a break in the shock adiabat for iron has been noticed for the first time[3] at 13 GPa which is the first evidence for a possible change in the structure of the substance during shock compression.

The methods used to measure shock adiabats are based on the measurement of the velocity of the wave front $D$ and the mass velocity of the test substance behind the front $u$ (in practice measurements are made of the velocity of the free surface of the specimen, which is close to twice the mass velocity). Knowing these kinematic parameters of the SW, it is possible to determine the thermodynamic characteristics of the substance (its density $\rho = 1/V$, the pressure $P$, and the increase in specific internal energy $\Delta E$) from the laws of conservation of mass, momentum, and energy:

$$\rho=\frac{1}{V}=\rho_0\frac{D}{D-u},\quad P=\rho_0 Du,\quad \Delta E=\frac{1}{2}P(V_0-V)$$

$D$ and $U$ are measured with the aid of electrical contacts in the central part of the specimen which is unaffected by stress relaxation waves (for the details of the method, see Al'tshuler's review[1]).

Careful investigations of the dynamic compressibilities of complex inorganic compounds have been carried out at the Institute of Chemical Physics of the USSR Academy of Sciences since 1957. Many such compounds have very high dynamic yield points—up to 10 GPa and above. The propagation of elastic waves with such amplitudes precluded the investigation of the compressibilities of such substances in the monolithic state over a wide pressure range by the methods known at the time, based on the measurement of the velocities of the SW and of the free surface. A "mixed" method,[4] based on the study of the compressibility of a mixture of particles of the test substance in a plastic medium, for example, paraffin, the shock adiabat for which is known, was therefore proposed and applied. This method made it possible to investigate the volume dynamic compressibilities of stable substances such as crystalline quartz,[5] glass,[6] and feldspar[7] also at low pressures.

In order to investigate the complex structure of the SW front in the elastic-plastic region or in phase transitions, an electromagnetic method,[6] previously employed to measure the velocities of the detonation products, was applied. This method made it possible to follow the evolution of the complex wave structures as they are propagated in glass,[6] potassium bromide and chloride,[8] and fused quartz.[9]

The investigations showed that all the substances mentioned above as well as marble[10] undergo structural changes during compression, i.e. in a period shorter than $10^{-6}$ s. The study of the impact compressibility of graphite[11] demonstrated that this important substance exhibits an anomalous compressibility at pressures of 20–40 GPa, which was interpreted as its conversion into diamond. The break at 60 GPa, caused, according to the authors,[11] by the transition of carbon to a metallic state, is a result of a methodological error, which was demonstrated in later investigations, for example, those of Pavlovskii and co-workers.[12,13] This erroneous result served as a basis for the construction of a phase diagram for carbon[14] in the region of high parameters which unfortunately has been used in the past by many investigators.

The aim of the above method was not to preserve the specimens: after recording a particular parameter, the specimen of the test substance disintegrated and was lost. For this reason, although these methods do in fact yield information about the pressure range in which the state of the test substance changes, about the structure of the SW front, and about the change in the electrical and optical parameters of the test substance, we obtain in essence only indirect data about the reactions which the test substance has undergone. These reactions are responsible for the anomalous behaviour of the shock adiabats observed for a whole series of substances.[3–16] In the first studies[3–11] it was already found that the anomalies on the shock adiabats, associated with the possible structural transformations in the test substances, occurred at relatively low pressures in the range 10–40 GPa, at which the preservation of the specimens was entirely possible; further studies were therefore developed with the aim of creating special devices (preservation tubes).

The difficulty of preserving the specimens after shock compression, particularly at ultrahigh pressures, is due to the presence in the decompression waves of powerful extending stresses which lead to the rupture of metallic containers and the loss of the test specimens. In constructing the retaining devices, the main task is to discover the region of the working volume within which the decompression waves do not interact and there is no appreciable macroplastic deformation. The appropriate positioning of the tubes with the specimens largely determines the success in devising preservation methods.

The first studies on substances preserved after impact compression were published at the end of the 1950's. In the first place one should mention the investigation[17] of the physicochemical transformations of substances under the influence of SW. This communication describes experiments on the shock compression of substances placed in cylindrical preservation tubes. It was shown that compression resulted in the partial decomposition of paraffin, NaCl, $CuSO_4$, $MgCO_3$, and $Pb(NO_3)_2$; on the other hand, sulphur underwent a phase transformation. Other investigations of preserved substances revealed the decomposition $Fe_2O_3 \rightarrow Fe_3O_4$ with decrease in the valence of the metal[18] and the conversion of $SiO_2$ into an amorphous form.[19] An important result has been obtained:[20] after the shock compression of graphite in a cylindrical tube, a small amount of finely dispersed diamonds was isolated. The results of investigations of metallic specimens (iron, steel, copper, and aluminium) and certain other technically important materials, preserved after shock compression, have been published.[21,22] Studies on the strengthening and welding of metals by an explosion have also begun to develop since 1960 (see the relevant monograph[23]). Much attention has been devoted to the explosive pressing of powdered materials.

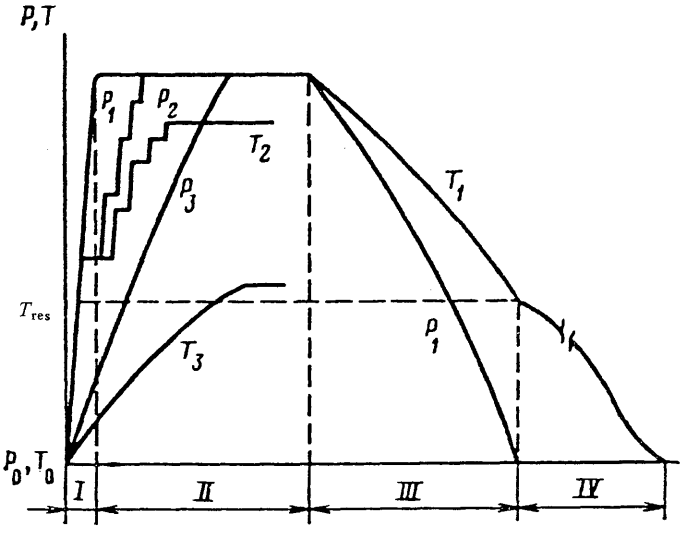



Figure 1. Idealised time variations of $P$ and $T$ at a certain point in the specimen in single ($P_1$, $T_1$) and multiple ($P_2$, $T_2$) shock compression and in dynamic isentropic compression ($P_3$, $T_3$). The rate of cooling of the substance along section III is not less than $10^8$ K $s^{-1}$.

In the studies quoted the experimental details and the conditions in the shock compression of specimens as well as the degree of macroplastic deformations of the tubes were inadequately described. The character of the interaction of the SW with the test substance had not yet been investigated at that time.

For a better understanding of the questions considered in this review, we shall deal with the general character of the changes in the pressure and temperature in the specimen in experiments with preservation, i.e. when the specimen is acted upon by the entire shock compression cycle, including rarefaction waves.

Fig.1 presents the idealised temperature and time variations of the pressure under the conditions of dynamic compression, by which we understand the compression of the test substance subjected to different types of stress; from compression by single-step and multistep SW to dynamic isentropic compression (DIS) or more precisely compression approaching isentropic compression. In the case of a single compression of the test specimen, the $P$ and $T$ increase simultaneously and very rapidly (over a period of $10^{-12}$ and $10^{-9}$ s) in the SW front (region I); the compression phase continues for $10^{-6}$ s (region II). The pressure is then removed by the isentropic decompression waves and (owing to the irreversibility of the shock compression) the temperature diminishes to a certain value $T_{res}$ (region III). Further cooling of what is now an unstressed specimen takes place in accordance with the usual thermal conductivity laws (region IV). The high residual temperatures in region IV can lead to the liquefaction (annealing) of the phase formed on compression and (or) to the occurrence of chemical reactions.

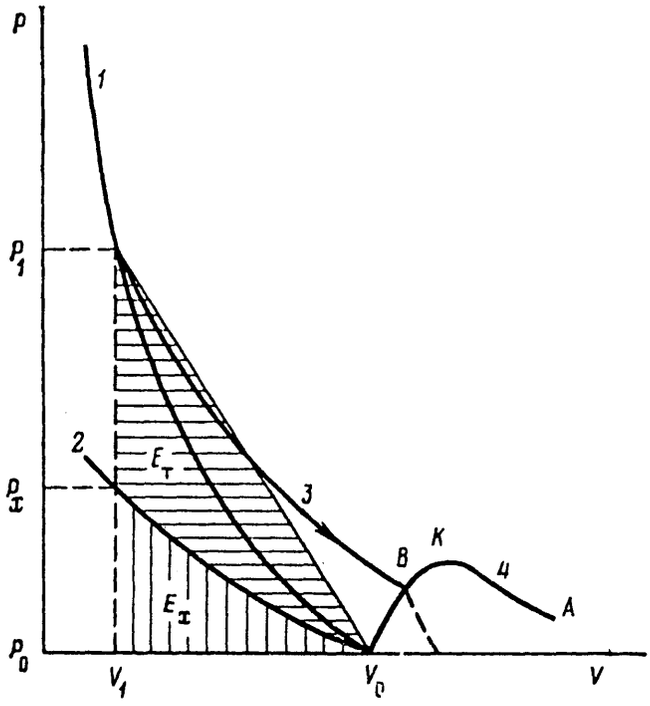



**Figure 2.** The $P-V$ relation on shock compression of the test substance and its relaxation: *1*) shock adiabat; *2*) cold (elastic) compression curve; *3*) rarefaction adiabat. The shaded regions correspond to the cold ($E_c$) and hot ($E_h$) components of the total energy of the compressed specimen; *4*) curve separating the regions of the single- and two-phase states of the substance.

Fig.2 illustrates the shock adiabat (curve *1*), the cold compression curve (curve *2*), the decompression adiabat (curve *3*), and curve *4* separating the regions of single-phase and two-phase states of the substance; its $V_0K$ branch before the critical point $K$ represents the boiling point curve (the onset of vaporisation) and the branch $KA$ represents the saturated vapour curve (the onset of condensation).

If the amplitude of the SW is not high, then, as a result of compression, the test substance passes from the initial $P_0V_0$ state to, for example, the state $P_1V_1$ (Fig.2). After decompression, the states of the system follow the isentropic decompression curve [shown by an arrow in Fig.2 (curve *3*)], which intersects the boiling point curve at point $B$, after which the solid should, in principle, boil. However, the rate of this process is negligible at temperatures of the order of hundreds and even thousands of degrees (for metals) and in reality the solid expands and cools to zero pressure along the "superheated liquid" adiabat shown dashed in Fig.2.

If the SW is very powerful and the internal energy of the heated substance is many times greater than the bond energy between the atoms (equal to the heat of vaporisation at $T = 0$), then, following its expansion to $P = 0$ in the region below the point $K$, the substance can completely vaporise. This problem has been analysed in detail in a book[2] (p.550).

Various designs of the preservation tubes for the dynamic compression of condensed substances with the aim of carrying out various physicochemical transformations are examined below. Attention has been concentrated on the conditions in the compression of the test substance following the application of different kinds of stress; certain results illustrating the possibility of the method based on dynamic influences are presented.

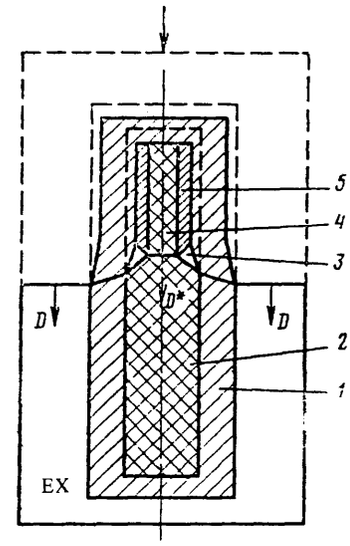



**Figure 3.** Schematic diagram of the compression of a substance in a cylindrical tube; $D$ = rate of detonation of explosive (EX); $D^*$ = rate of propagation of head SW: *1*) metallic tube; *2*) test substance; *3*) and *4*) regions of single compression behind the front of the incident and head SW; *5*) region of double compression behind the front of the incident and reflected SW. The dashed lines indicate the initial positions of the explosive, the tube, and the specimen.

## II. THE BEHAVIOUR OF SUBSTANCES COMPRESSED BY CONVERGING WAVES

Cylindrical preservation tubes are the principal means of carrying out dynamic experiments for chemical purposes. Fig.3 illustrates a cylindrical metallic tube and the test

substance placed in it; the tube is arranged along the axis of the explosive charge. As a result of the detonation of the explosive, the detonation wave passing around the cylinder excites a conical converging shock wave in it and in the test substance. The wave undergoes a transition to a three-shock configuration which is propagated in the stationary region at a rate equal to the rate of detonation of the explosive employed.[24] The three-shock configuration arises in solid (continuous and porous) substances and in liquids.

The details of the investigation have shown[25] that there is a linear relation between the diameter of the head wave (the Mach wave), occupying the central part of the three-shock configuration, and the diameter of the specimen. It is significant that in the central part of the tube the test substance undergoes a single shock compression by the head wave, while at the walls of the tube it undergoes a double compression by the incident and reflected SW; as a result of this, for the same final pressure, the shock heating of the test substance in the centre of the specimen is much greater than at the walls of the tube. The compression conditions also differ along the length of the specimen. It is almost always possible to differentiate three zones: the region where a three-shock configuration is produced, the region of the stationary propagation of the wave, and the region at the bottom of the tube where additional compression of the test substance by the SW reflected from the bottom can take place. Thus in a single experiment the substance located in different zones of the cylindrical specimen is subjected to stresses of different kinds.

The observed relation between the rate of propagation of the three-shock configuration and the rate of detonation of the explosive charge employed made it possible to determine the pressures developed without special direct measurements (when the shock adiabat for the test substance is known). It was found that it is very simple to achieve pressures of several hundreds of GPa. Thus the use of an explosive whose detonation velocity is $\sim 8 \times 10^3$ m s$^{-1}$ generates maximum pressures of ~500, 60, and ~35 GPa in monolithic specimens of tungsten, sodium chloride, and perspex respectively. In order to increase the pressure, for example, in salt, it is sufficient to mix and compact tungsten and salt powders. With a low sodium chloride content, pressures close to 500 GPa can be reached as a result of repeated compression and equalisation of the pressure in the specimen.

The next important factor was the occurrence of very intense plastic deformations in the working volume of the cylindrical tubes with axial filling.[26] The particles of the test substance can migrate under such conditions relative to one another over considerable distances in the direction of propagation of the three-shock configuration, particularly in the central part of the tube. Evidently such conditions should promote the decomposition of chemical compounds, should significantly accelerate the fusion processes, and should facilitate chemical interactions of substances. An attempt has been made to separate the decomposition products using intense plastic flows.[26] For this purpose, a very small amount of the test substance (0.5 wt.%), for example, an oxide, was mixed with ground quartz and the mixture was subjected to shock compression. After the experiment the metallic shell was dissolved in hot hydrochloric acid and the remaining monolithic quartz bar was ground and polished. The ground sections were investigated under a microscope. This method revealed traces of the movement of the particles of the material of the tube into the test specimen and also traces of plastic deformations shown by a change in the colour of the test substance following the chemical reaction. In order to protect the test substances from contamination, quartz or glass inserts were used, which completely prevented the migration of the contaminant into the specimen. It was shown in these experiments that, during the plastic flows in the preservation tubes under shock compression, the particles of the test substance can migrate in the direction of the SW over a distance of 2–3 and more centimetres.

The behaviour of more than 60 oxides has been investigated by this method under identical shock compression conditions. Special measurements showed that in porous quartz ($\rho_0 = 1.48$ g cm$^{-3}$) and hence also in the test oxides a pressure of ~48 GPa developed; the concentration of energy was then $E = 1.2 \times 10^4$ kJ kg$^{-1}$. The capacity of oxides for decomposition under shock compression was determined by the enthalpy $\Delta H^0_{298}$ of the process involving the elimination of one gramme-atom of oxygen. Oxides with $\Delta H^0_{298}$ ranging from 62.8 kcal g-atoms$^{-1}$ ($Ag_2O$) to 211.0 kcal g-atom$^{-1}$ (CaO) were investigated. It was found that the decomposition limit of the substance subjected to the influences indicated corresponds to a quantity which is only 20% below the overall energy of the shock compression.[26]

In order to ensure the chemical purity of the experiments, it was necessary to determine the degree of contamination of the test substances by the materials of the walls of the tubes as a function of the properties of the substances and the conditions of the dynamic influence. For this purpose, the contamination of sodium chloride and alumina, placed in steel-65 tubes, was determined by chemical analysis. Sodium chloride was used in the form of a powder or was fused *in vacuo* on the inner part of the tube. After the experiment, the tube was opened, the test substance was extracted, and the distribution of iron along the length and radius of the tube was investigated. The results showed that, when the test specimen is monolithic, then the material of the walls hardly penetrates the test substance. On the other hand, if the tube is filled with a powder, particularly one which is difficult to compact, such as $Al_2O_3$ (in the experiments the initial density of $Al_2O_3$ was 1.1 g cm$^{-3}$, while that of powdered NaCl was 1.9 g cm$^{-3}$), then the degree of contamination of the specimen by iron reached several tenths per cent.[27] In the above study it was shown that, if for any reason, it is not possible to employ a monolithic specimen, then one can subject the specimen to preliminary impact compression using the detonation of a low power explosive charge which causes only an insignificant contamination of the test substance but ensures its effective compaction. At the same time a sharp decrease of the maximum temperature developed on repeated compression is achieved, because the specimen had been subjected to preliminary compaction.

The influence of SW on porous substances as a rule leads to the formation of more or less monolithic cylinders having in most cases a characteristic structure: along the axis, there is a filamental cavity 0.1–0.5 mm in diameter. Its formation is due to the interaction of the rarefaction waves. A cavity 1–3 mm in diameter is sometimes formed in the lower part of the specimen.

Under certain conditions (high pressures and a low crystal lattice energy of the test substance), the substance may not only melt but may evaporate at the centre of the tube. The migration of the test substance in the direction opposite to that of the propagation of the SW has been demonstrated by the radioactive isotope method.[28]

After the completion of the process, a characteristic microstructure, usually arising during the radial crystallisation of the fused metal in the tube during its uniform external cooling, can arise throughout the volume of the cylindrical specimen. This feature of the shock compression of the test substance in cylindrical tubes is associated with the difference

between the residual temperatures of the substance and the walls of the metallic tube. This difference is particularly large in the study of specimens in a porous state where the residual temperature of the substance can reach several thousands of degrees, while that of the metallic tube is hundreds of degrees. As a result, conditions are created for the rapid cooling and quenching of the test substance. For example, estimates for niobium pentoxide have shown[29] that the total crystallisation time of the melt is ~0.3 s, while the linear rate of crystallisation is 0.05 m $s^{-1}$; for tungsten, these quantities are 0.005 s and 0.3 m $s^{-1}$ respectively.

In most cases specimens with a reduced density, whose pores contain air at atmospheric pressure, are investigated in cylindrical tubes. One can assume that during the shock compression of such systems with a small particle size $k$, the pressure is equalised but thermal equilibrium is not established. Owing to the small weight fraction of air, its contribution to the temperature is small and the average temperature of the mixture differs little from that of the solid component, although in the initial instant of the compression the air in the pores was heated to a much greater extent. After intense shock compression, the porous medium undergoes a major volume deformation and hence is heated more than a continuous substance compressed to the same final pressure.[1] Even after the shock compression of porous specimens subjected to preliminary evacuation the temperature developed may amount to tens of thousands of degrees and part of the substance passes to the state of plasma;[30] thermal emission of electrons can take place under these conditions.[31]

The shock compression of porous substances does not entail major difficulties in the solution of the problem of the preservation of the compression products. Difficulties arise when the test substances decompose or react with the evolution of a large amount of gas and especially when the pores have been filled beforehand with gases which have been compressed to high pressures or liquefied. As a rule, the usual tubes are ruptured under these conditions by the high internal pressure. In order to preserve the tube without rupture, it is necessary to develop special designs. Evidently the preservation of the tube should be promoted by the situation where the gas reacts partly or fully with one of the components of the specimen on compression to form a solid product. It has been shown[27] that the compression of the oxides, fluorides, chlorides, iodides, and sulphates of univalent, bivalent, quadrivalent, and hexavalent elements did not lead to the rupture of the tubes. Comparatively readily decomposed substances such as copper sulphate, barium chloride dihydrate, paraffin, phosphorus oxide nitride, and nickel fluoride hydrate and substances which are highly volatile under the usual conditions such as sulphur and mercury were also satisfactorily preserved in specially developed tubes. The tubes were preserved without rupture also on compression of the substances listed below. Far-reaching hydrolysis on shock compression of nickel fluoride hydrate resulted in the evolution of a considerable amount of free water and hydrogen fluoride; phosphorus oxide nitride decomposed almost completely into nitrogen and phosphorus and layer phosphorus oxides, and copper sulphate partly decomposed to free copper.

Systematic studies have been made to develop cylindrical preservation tubes which would permit the shock compression of solid–condensed gas mixtures in order to carry out various chemical interactions.[32] The task of preserving condensed gases after their compression in SW involves considerable difficulties. Firstly, metals become brittle at low temperatures, which increases the probability of the rupture of the tubes. Secondly, the high compressibility of condensed gases leads to considerable deformations of the tubes on compression and decompression which leads to the rupture of the tube under the conditions of increased brittleness of the material. Thirdly, even if the liquefied gas does not vaporise during compression, the effect of high residual temperatures after rarefaction causes its transition to the gaseous state, which creates high pressures within the tube capable of rupturing it. However, special tube designs, providing for the removal of the excess gases, made it possible to preserve the solid product. As a result of the investigations carried out, the interactions of various substances with liquid nitrogen and solid carbon dioxide have been achieved. In particular, the possibility of the formation of niobium nitride and carbide on shock compression of a mixture of powdered niobium with liquid nitrogen and carbon dioxide has been demonstrated.[32] The interaction of various metals with hydrogen yielded hydrogen-containing titanium and manganese compounds as well as other substances. It has been shown that saturated hydrocarbons and water can be used as sources of hydrogen in such interactions.[33]

In order to obtain $CO_2$ in the solid state under normal conditions, attempts have been made to oxidise SiC under the conditions of shock compression.[34] Mixtures of powdered SiC with gaseous or liquid oxygen were subjected to shock compression in preservation tubes. The study of the compression products by X-ray diffraction and infrared spectroscopy showed that the interaction of oxygen with SiC involves the oxidation of the latter and the formation of a non-molecular lattice structure. Heating of oxidised SiC to 800–1300 K removes carbon oxides. The cylindrical tube can be improved; in order to simplify the pattern of wave interactions and to eliminate the head wave, it is sufficient to insert a metallic rod along the axis of the tube. In this case the specimen in the form of a cylindrical layer is subjected to shock compression. This design can be used to achieve structural transformations[35] and also in technological processes—for the pressing of tubes.

Thus the generation of very high pressures, temperatures, and macroplastic deformations of specimens in cylindrical preservation tubes has a positive influence on many physicochemical processes. However, these conditions and the complex pattern of wave interactions in the test specimens restrict the scope of studies of the behaviour of substances under dynamic compression, whose class is limited mainly to metals and refractory compounds.

## III. PLANAR DYNAMIC COMPRESSION

The creation of devices for the preservation of substances subjected to compression by planar SW ensured the possibility of dynamic compression at a lower maximum pressure but with a simpler pattern of wave interactions than in the cylindrical scheme. Planar compression also has the advantage over compression by converging waves because the SW parameters are susceptible to measurement and the compression conditions are controllable.

### 1. Experimental Technique

Fig. 4 illustrates schematically the designs for the preservation of substances after shock compression using a planar compression scheme. The shock waves in the tube and in the specimen are generated by a planar detonation wave of an explosive charge in contact with the tube (Fig. 4*a*) or as a result of the impact of a metallic

plate accelerated by the detonation product (Fig.4*b*).[33] After an appropriate selection of experimental conditions, the shock compression pressures in the test substance and in the material of the tube are equalised by repeated reflections of the SW from the bottom and lid of the tube when the latter is made of a material whose dynamic rigidity is greater than that of the test substance.[33] The scheme in Fig.4*b* is more convenient because impact by plates generates SW with a rectangular profile. A change in the thickness of the impact plate makes it possible to measure or calculate more rigorously the residence time of the test substance in the compression phase. In order to obtain more information, several specimens of different test substances were placed in a planar cassette (Fig.5*b*), which was in its turn inserted in the tube (Fig.5*a*), which made it possible to study the behaviour of different substances in a single experiment under comparable conditions. Such formulation of the experiment permits in addition the variation of the number of reflections of the SW in the specimen by using different thicknesses of the latter (Fig.5*c*).

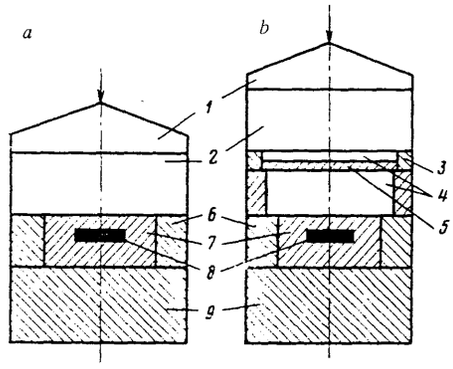



**Figure 4.** Schematic illustration of devices for planar shock compression: *1*) generator of planar detonation wave; *2*) explosive charge; *3*) metallic ring; *4*) air gaps; *5*) impactor; *6*) protective ring; *7*) tube; *8*) test substance; *9*) metallic support.

The pressures developed in the specimens depend on the dynamic rigidity of the material of the tube and the compression conditions and can range from 1 to 150 GPa.[33]

Despite the simpler compression pattern of the test substance when planar SW are used compared with the cylindrical compression scheme, the determination of the characteristics of the substance as a function of pressure requires a larger number of independent experiments with preservation of the specimen, also the compression conditions can be different in different experiments. A method has therefore been developed whereby it is possible to achieve in a single experiment the shock compression of one or several different substances over a wide range of fixed pressures with subsequent preservation of the specimens for physicochemical analyses.[36] Under the conditions created in this method, as the SW is propagated in a metallic block, the maximum pressure and temperature fall sharply after the wave has travelled a relatively short distance. A calibration relation between the pressure and the thickness of the metallic layer has been determined with the aid of special measurements.

The shock wave was generated in a copper block by the impact of an aluminium plate 1 mm thick accelerated by the products of a planar detonation of a thin layer of explosive; the distance traversed by the impactor was 2.5 cm. (We may note that at 45.5 GPa the maximum temperature of the copper reached 670 K, while the residual temperature $T_{res}$ (Fig.1) was 480 K; at 13.2 GPa the corresponding temperatures were 380 and 330 K respectively.) The metallic block was then replaced by a set of plates of the required thickness, between which thin specimens of the test substance were placed. They were subjected to repeated shock compression at different fixed pressures.

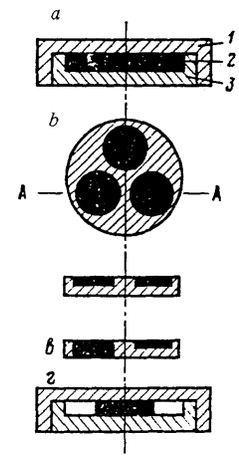



**Figure 5.** Design of the preservation tubes: *a*) preservation tube: *1*) lid; *2*) test substance; *3*) bottom of tube; *b*) cassette with three specimens which can be inserted in the tube instead of specimen *2*; *c*) section through the cassette along the AA line; *d*) preservation tube permitting a specified degree of deformation of the specimen as a result of its movement into the free volume on compression.

Comparison of the data obtained for the compression of the test substance in a layered container of this kind, where the shock compression times are short, with data obtained in independent experiments at the same pressures but for specified and longer compression times made it possible to obtain the dependence of the physicochemical characteristics on the shock compression time. In the experiment described the duration of the compression phase was determined from the instant of the appearance of the rarefaction wave arriving from the direction of the impactor; the pressure decreased over a period of 1.5–2.0 μs.

The specimens of the organic substances investigated, in the form of discs up to 0.7 mm thick at 15 mm in diameter or in the form of plates 50–100 μm thick, were placed within sockets in copper plates or were positioned between plates. In each layer several specimens of different substances could be placed. By selecting copper plates of a suitable thickness, it is possible to obtain up to 15 maximum pressures in the SW in the range from 10 to 40 GPa for several test substances in a single experiment. Since the thicknesses of the specimens are small, one can assume that there is no significant distortion of the wave front. The final pressure in the specimen after repeated compression is close to the

pressure in the copper plate, since the time of a single pass of the SW through the specimen is ~0.02 μs.

It is noteworthy that the contact of the thin layer of the test substance, which has been more compressed and heated to a higher temperature, with the metal heated to a lower temperature promotes the rapid removal of the residual heat from the specimen, ensuring a kind of quenching. Estimates have shown that, when a layer container is used for the shock compression of specimens of organic substances ~100 μm thick, the time required to equalise the temperature between the specimen and the metal is ~0.35 s. This design permits experiments at an initial temperature of 77 K, which improves the quenching conditions.

The planar compression scheme was used to study various substances and processes on shock compression. It proved to be most useful in the investigation of substances with a low thermal stability, such as, for example, organic substances.

## 2. Chemical Reactions of Organic Substances

Studies on the chemical reactions in organic substances which have undergone shock compression were initiated at the Institute of Chemical Physics of the USSR Academy of Sciences in 1965. The experiments performed using planar compression schemes revealed,[37] and this was subsequently confirmed in relation to many monomers, that exposure to a shock wave induces rapid polymerisation.[38] Polymerisation was observed for different classes of monomers which usually polymerise via radical (acrylamide) or ionic (trioxan) mechanisms. In addition, many monomers (tolane) which are extremely difficult to polymerise under the usual conditions do polymerise in the SW. The investigations showed that polymer chains are formed when the amplitude of the SW reaches a specific value, which differs for different monomers. The yield of the polymer formed and its average molecular weight initially increase with the SW amplitude and then diminish owing to the thermal degradation of the polymers. With increase of pressure, not only the length of the macromolecules changes but there is also a possibility of a change in the structure of the polymer chain. It has been shown[38] that these chemical reactions under the influence of SW cannot be reduced to a trivial thermal process and fusion or to a combination of static compression and heating.

The possibility of the formation of macromolecules as a result of polycondensation has also been considered. It has been demonstrated that the action of a SW in a mixture of α-aminoacids with silica gel can entail the formation of polypeptide molecules.[39] The authors[39] attribute a dehydrating role to silica gel, which displaces the reaction equilibrium towards the formation of polypeptides.

The first studies on the effect of SW on polymer systems (butadiene–nitrile, butadiene–styrene, natural and other raw rubbers) showed that in this case there is a possibility of the cross-linking of the macromolecules with formation of a three-dimensional network and their partial degradation.[40,41] The study of polymers with saturated bonds, such as poly(metyl methacrylate), polypropylene, polyethylene, and polystyrene showed that, regardless of the initial supermolecular structure (spherolitic, fibrillar, and quenched structureless) the effect of the SW leads to the formation of an isotypical fine spherolitic structure.[42] The use of a layer container permitted the study of the structural changes in polymer films at pressures differing by only 1.0–1.5 GPa in the range 10–40 GPa.[43] It was shown that the transition to the fine spherolitic structure takes place at pressures of 13.5, 23, 25, and 27 GPa for polybutylene, polypropylene, polyacrylonitrile, and Lavsan respectively. The degree of deformation of the specimens was estimated from the relation $\varepsilon(\%) = 100(R - R_0)/R_0$, where $R_0$ and $R$ are the radii of the specimen before and after shock compression: it did not exceed 1%. Comminution of the supermolecular formations and an increase of the microhardness in the surface layers have been noted in a study[44] of the shock compression to 10 GPa of crystalline polycaprolactam and amorphous poly(methyl methacrylate).

A more detailed analysis of the above results was carried out in other investigations.[45,46] The efforts of many investigators, mainly Soviet scientists, were subsequently directed towards a more detailed study of the physicochemical properties of organic substances subjected to shock compression in preservation tubes and towards the elucidation of the mechanisms of the chemical reactions which occurred.

Three fields of study have now arisen. Firstly, we have the investigation of the reactions of low-molecular-weight organic substances, which include isomerisation, for example, the conversion of *trans*-stilbene into *cis*-stilbene,[47] condensation—the formation of polypeptides from α-aminoacids,[39] the dimerisation of polynuclear compounds such as anthracene, phenanthrene, and pyrene,[48] intramolecular rearrangements, for example, the formation of poly-β-alanine together with the usual vinyl polymerisation of acrylamide,[49] and finally the degradation reactions which partly accompany the processes enumerated above.

The data on the degradation of aromatic and cyclic compounds by SW proved to be the most informative.[50,51] It has been shown that shock compression of benzene disrupts the benzene ring and leads to the formation of a considerable amount of ethane and hydrogen, greatly exceeding the amount of the degradation products formed on compression of the less thermally stable hexane and cyclohexane. The authors of these investigations suggest that the disruption of the molecular structure is of a non-thermal character and that a change in the valence angles in the rigid benzene ring is impossible without the breakdown of the latter. On the other hand, aliphatic groups in cyclohexane can undergo a change in valence angles with subsequent relaxation. It has been concluded that the decomposition of benzene molecules takes place directly in the SW front where the most intense microplastic deformations take place.

Presumably the formation of defects, active centres, etc. in the SW front constitutes the "initiating" stage of the subsequent reactions. The isomerisation and condensation reactions can also be considered from this standpoint.

The second field of study involves the investigation of polymerisation reactions and demonstration of the activating role of the SW front in this process. The initiating role of the SW front in the polymerisation of acrylamide (AA) under the conditions of shock compression was first noted by Adadurov et al.[52] The experiments were performed at 77 K and a pressure where the polymer is not yet formed. Next, when not more than 30 s had elapsed since the experiment, the tube was cooled with liquid nitrogen, opened at this temperature, and the physicochemical analyses of the specimens were begun also at 77 K. The presence of active polymerisation centres at a concentration of $10^{20}$–$10^{21}$ $kg^{-1}$ in the compressed AA specimens was confirmed by EPR. The SW front was regarded as a generator of active centres. The subsequent rise in the temperature of the SW-activated specimens led to an explosive AA polymerisation process, which was investigated calorimetrically. The data obtained and calculations led to the conclusion[52] that, depending on the temperature conditions established in the compression stage and obtaining after the removal of pressure, polymerisation can take place

either as a slow after-effect or as a thermal explosion. At high shock compression pressures, accompanied by the development of high concentrations of active centres and high temperatures, the polymer can be formed in the compression stage during a period shorter than $10^{-6}$ s. The presence of active polymerisation centres in AA compressed by a SW of brief duration has been confirmed by EPR.[53] The polymers were formed on subsequent dissolution of the specimen in tetrahydrofuran.

γ-Irradiation of the majority of solid monomers at low temperatures is known to lead to the formation of stable active centres which initiate the polymerisation process on subsequent temperature rise. A study has been made[54] in which AA specimens γ-irradiated in doses up to 6.3 Mrad were subjected to shock compression at 16 GPa and 77 K. It was shown that, for the dose indicated, the yield of the "purely radiation" polymer was 20%. The shock compression of non-irradiated AA led to the formation of 5% of the polymer, while that of the irradiated AA afforded 40% of the polymer. This yield exceeds by a factor of almost 2 the simple sum of the contributions by both influences and is almost an order of magnitude higher than the yield of the polymer due to the action of the SW alone. In the next Section of the review, in the analysis of new possibilities in dynamic investigations, direct proof of the decisive role of the SW front in the polymerisation of AA will be given.

We may note that the polymerisation mechanism under the conditions of shock compression described above is not the only one possible. Thus study of the polymerisation of trioxan[55] showed that the structural changes in the monomer during the compression stage are decisive for the formation of polyformaldehyde. The propagation of trioxan chains in microcrystalline and single crystal specimens has been investigated[56] as a function of the variable pressure and duration of the shock compression. It was concluded that the polymerisation takes place during shock compression and that the growth of polymer chains is virtually limited to this period. An increase of pressure entails an appreciable acceleration of the chain growth. The polymer chain propagation process is influenced significantly by the degree of perfection of the crystal lattice. Analysis of the changes in the characteristics of the products of the polymerisation of single-crystal trioxan under different conditions of compression by SW [57] showed that the molecules undergo a deformation which accelerates all the stages of the polymerisation process. Active centres are formed on partial degradation of the monomer molecules in the SW front, whereupon their number increases with increase in the degree of deformation.

The study of the transformations in polymers subjected to shock compression can be regarded as the third field of study. The observed degradation and cross-linking reactions[40,41] can also be accounted for from the standpoint described above in connection with the consideration of the mechanism of the polymerisation reaction. It is noteworthy that the long chains in the polymer macromolecules should be more sensitive to deformations in the SW front and the breaks in these chains should entail the formation of radicals. The subsequent reactions of these radicals can lead either to the degradation of the macromolecules or to their cross-linking with formation of a three-dimensional structure depending on the characteristics of the polymer, the presence of double bonds in the chain, etc.

In the study of the changes of the supermolecular structures of polymer specimens subjected to shock compression, the radiothermoluminescence (RTL) method was resorted to in addition to optical microscopy and X-ray diffraction.[43] Polypropylene (PP), in which any initial structure is converted into a fine spherolytic structure at a threshold pressure of 23 GPa, has been studied in greatest detail. It has been shown by the RTL method that, at a pressure below the threshold value the crystal structure breaks down and the fraction of the amorphous phase increases. It has been suggested that the compression in the SW front induces the formation of defects in the polymer structure and the annealing of defects or the rearrangement of the supermolecular structure at the elevated residual temperatures increases the fraction of the amorphous phase. The low-temperature luminescence peak observed by the RTL method for PP specimens compressed at 77 K indicates the possibility of the breakdown of the supermolecular structures. This low-temperature transition can be due to the local relaxation of the ends of the macromolecular chains along the boundaries of the cracks formed and on the surfaces of the lamellae. It has been suggested that the structural changes take place in polymers "activated" by the SW front immediately after the removal of pressure owing to the effects of the residual heat and can only be interpreted when account is taken of all the factors accompanying shock compression.

Studies of the chemistry of the shock compression of organic substances in which the observed effects were also explained have been published in recent years.[58-60] The conclusions reached are close to our ideas described above and reduce to the fact that shock compression can induce chemical reactions, including unusual reactions, which cannot occur for equivalent combinations of static pressures and temperatures and that the reactions can take place in the SW front itself. It has been suggested that the "anomalous" effects can be the result of "catastrophic shock".[58] According to this concept, the shock waves generate a high concentration of defects and cause the mechanical rupture of chemical bonds and the relative displacement of neighbouring groups in the SW front. As in the present author's investigations discussed above, the author[58] states that much more attention should be devoted to the possible processes in the SW front, such as the generation of a non-equilibrium state and defects, the breaks in chemical bonds, etc.

## IV. THE REALISATION OF SPECIFIED THERMODYNAMIC CONDITIONS IN THE DYNAMIC COMPRESSION OF CONDENSED SUBSTANCES

The interrelation between the pressure in the SW front and the temperature developed there, limits the possibility of achieving sufficiently high pressures without the accompanying marked heating of the test substance. Shock compression of a precooled substance also does not lead to an appreciable reduction of this temperature. In other words, the region of the $P-T$ diagram immediately adjoining the $P$ axis is in principle inaccessible in experiments with SW.

The attainment of this region under the conditions of dynamic compression at pressures up to 100 GPa and above is essential for the study of the metallation of dielectrics, including condensed gases, for the reduction of residual temperatures after intense dynamic compression, and for the prevention of the annealing of the high-pressure phases formed and the decomposition of the newly formed chemical compounds, etc. Despite certain advances in the technique of high static pressures, at the present time pressures in excess of 50 GPa can be obtained only on compression of extremely small amounts of test substances. Under dynamic conditions, the above restrictions are not limiting.

### 1. Stepwise Compression and Dynamic Isentropic Compression

The possibility, in principle, of a decrease in the temperature rise of the test substance on shock compression by organising a stepwise compression of the specimen by a series of successive SW of lower amplitude is known from the SW theory. For the same final pressure, the final temperature of the specimen is reduced in stepwise compression and the degree of compression of the test substance increases (because of the decrease of the thermal component of the pressure). As a result, the states located on the shock adiabat for repeated stepwise compression should approach the states on the compression curve at the absolute zero. Experiments in which shock adiabats have been recorded with double shock compression of certain substances have been described in the literature. An X-ray diffraction method for the investigation of regular regimes involving the oblique reflection and oblique collision of SW as well as the head on collision of SW introduced to achieve the double compression of magnesium, aluminium, perspex, paraffin and water have been described.[61] It has been shown that double compression states correspond to comparatively low temperatures and small thermal components of the pressure. For example, double shock compression of aluminium to a density of 1.57 g $cm^{-3}$ results in the heating of the specimen to ~1100 K; on the other hand, in a single compression to the same density, the temperature reached is ~3800 K. The thermal components of the pressure in single and double compressions reach 20 and 6 GPa respectively.

P–V diagrams have been determined[62] for marble subjected to double shock compression. The shock wave emerging from marble was reflected from a copper plate with a high dynamic rigidity and was propagated through the marble specimen already subjected to compression by the first wave. It has been shown that at pressures in excess of 15 GPa the state arising in double compression significantly differs from the state in single compression and approach the "cold" compression curve.

It is seen from the examples presented that double shock compression makes it possible to reduce the temperature developed in the test substance. Repeated SW compression or "smooth" dynamic compression should make the process even closer to an isentropic process. Repeated SW compression of water and boron nitride to pressures of 100 GPa has been carried out[63] in order to measure their electrical conductivities. The compression of test specimens placed between two copper plates was achieved by creating shock counterwaves of identical amplitude, which were generated by the synchronous collision of aluminium plates accelerated by the explosion products. It was shown in these experiments that in the region of 80 GPa boron nitride exists in a semiconducting state. The electrical conductivity of water is ionic and at a pressure of 30 GPa the specific conductance reaches a plateau as a result of the attainment of the total dissociation of water molecules.

The dynamic isentropic compression (DIS) of fused quartz and liquid hydrogen to ~500 GPa has been achieved[64] with the aid of an explosive magnetic flux compression technique. It was shown that, up to pressures of 500 GPa, quartz does not become an electrical conductor. At 200 GPa liquid hydrogen has a density of ~1 g $cm^{-3}$ and at this pressure its transition to a metallic state was not observed. The density of hydrogen subjected to repeated shock compression has been measured[65] by the $\gamma$-ray diffraction method; the density was determined by measuring the diameter of a cavity converging towards the centre of a cylindrical shell (accelerated by detonation products) in which hydrogen was present initially in the gaseous state. It was shown that, at pressures in excess of 280 GPa, the density of hydrogen increases from 0.8 to 1.3 g $cm^{-3}$, which the authors suggest is due to the transition of hydrogen to the metallic state.

Several studies postulating various schemes (not realised experimentally hitherto) for the achievement of the isentropic compression of a substance under dynamic conditions have been published. Thus Yampol'skii,[66] who also carried out a general analysis of the state of the problem, suggested that the "smooth" compression of the specimen be effected by the products of the detonation of a charge located at some distance from the target; the period of increasing pressure then depends on the size of the gap. It has also been suggested that media with variable dynamic rigidities be employed. In the propagation of SW through such media there is a possibility of the transformation of the SW into a wave with a smooth increase of pressure in the front.[66] A gas-dynamic method for the low-temperature compression of solid hydrogen placed in a copper cooling conductor has been proposed.[67] The isentropic compression of hydrogen can be achieved in this method by transmitting pressure to the cooling conductor via a gas which is compressed by a metallic cylinder moving towards the centre as a result of being acted upon by a descending detonation wave.

All the proposed methods have been designed to record the low-temperature states of substances in the course of shock compression or DIS and do not provide for the preservation of the specimens of the test substances. In the above methods the test specimens break down after compression and fly apart in the form of a plasma, particles, fragments, etc. One should also note the difficulty and high cost of creating a cylindrical converging detonation wave and reproducible strong magnetic fields.[68]

### 2. The Generation of Low-Temperature States of Condensed Substances in Dynamic Compression in Experiments with Preservation of the Specimens

Systematic studies designed to generate experimental conditions ensuring low-temperature dynamic compression were initiated in 1970 at the Institute of Chemical Physics of the USSR Academy of Sciences. Attention was concentrated on the development of simple schemes for the compression of substances placed in preservation tubes and ensuring a closer approach to the isentropic regime compared with the stepwise shock compression.

Since the temperature on the isentropic curve corresponding to the given degree of compression is linearly related to the initial temperature of the test substance, it follows that, in order to be able to carry out experiments at lower temperatures, it was necessary to develop also designs for preservation tubes permitting experiments with the specimens cooled to 4.2 K. Evidently dynamic isentropic compression at low temperatures should lead to the appearance of states of the test substance which are located in the immediate vicinity of the compression curve at the absolute zero. Estimates have shown,[66] that, for example, in the shock compression of lead to 100 GPa, the maximum temperature reaches ~9200 K, while the residual temperature is 1800 K. Isentropic compression to the same pressure of the specimen initially at room temperature should heat lead by not more than ~900 K and from 4.2 K only up to 12 K.

We shall consider briefly below the principal experimental schemes developed for the achievement of low-temperature dynamic compression and shall discuss the differences in the states of various substances whose specimens were

preserved after repeated shock compression and after DIS.[33,69-73]

Analysis of the propagation of SW in media with variable density indicates the possibility of their transform ion into smooth isentropic compression waves.[63,73] Since it is very difficult to prepare a medium with a continuously varying medium density, systems consisting of layers of substances having different dynamic rigidities, which made it possible to reduce significantly the amplitude of the first SW and to increase the number of subsequent waves in the repeated SW compression of the test specimen, have been used.[69,70] Organic substances having low thermal stabilities were employed as a kind of thermoindicators.

In one of the methods proposed, a decrease of the amplitude of the first SW was achieved by placing a buffer system of plates (screens) made up of different materials in front of the specimen.[69] In these experiments it was possible to reduce the amplitude of the first SW in acrylamide and polypropylene to ~3 GPa for a final pressure of 50 GPa. In the case of repeated shock compression for the same pressure in the absence of screens, the amplitude of the first wave was ~13 GPa and for the specimen initially at room temperature AA underwent total thermal degradation and PP underwent a thermal structural transformation. On the other hand, under conditions close to DIS, i.e. in the presence of screens, there was only partial degradation of AA and the structural transformation of PP did not take place.

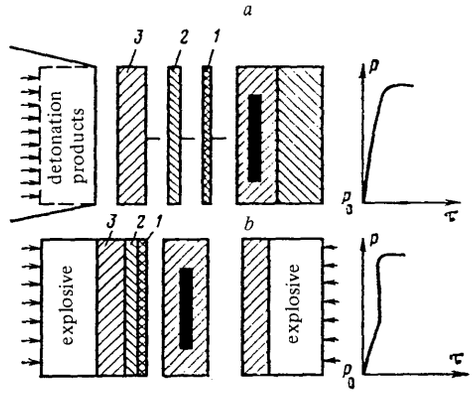



**Figure 6.** Schematic illustration of devices ensuring the dynamic isentropic compression (*a*) and successive compression of the test substance by the isentropic wave and then the shock wave (*b*); the three layer impactor is made up of perspex (*1*), aluminium (*2*), and copper (*3*) plates. The time variation of the pressure in the specimen during compression is shown on the right.

The compression scheme illustrated in Fig.6, which permits the achievement of "smooth" compression of the test substances placed in preservation tubes by successive impacts against the tube by plates (impactors) with increasing dynamic rigidity, proved to be the most rational.[33,70] By a planar detonation of an AA charge, SW are generated and propagated in this method over a system of plates, made, for example, of copper, aluminium, and perspex; when the shock wave reaches the free surface, it initiates at first the motion of the perspex plate, which acquires the highest velocity by virtue of its high compressibility. Impactors made of aluminium and copper require lower velocities and the velocity of the plate is lower the greater the dynamic hardness of its material. The final pressure in the target is generated after impact by the copper plate.

Qualitative analysis of this method leads to the conclusion that, when the distance between the layer impactor and the target is varied, it is possible to achieve a wide variety of different profiles of the compression waves accompanied by a longer period of increasing pressure at the given point in the specimen compared with the usual repeated SW compression. It is significant that, when the law governing the decay in the target (the lid of the tube) of the shock wave generated as a result of the impact by the first thin plate is known, it is possible to select the thicknesses of the materials in such a way that after the first impact the test substance is acted upon by a SW with a very low amplitude.

A series of experiments have been carried out[73] on the repeated shock compression and DIS of an organic monomer—acrylamide, using various compression schemes (Figs.4*b* and 6*a*), up to 40 GPa at initial temperatures of 293, 77, and 10 K. After the experiments, the tubes were cooled to 77 K in order to fix the products formed, then opened at the same temperature, and the properties of the specimens were investigated also starting with 77 K. It was found that repeated shock compression of AA at 293 K led to its complete degradation or at 77 K it gave rise to a 30% yield of the polymer. On raising the temperature of the cooled specimens, postpolymerisation was not achieved, apparently as a consequence of the annealing of the active centres. In the course of compression at 10 K, 10% of the polymer was formed and the concentration of active centres remained the same, so that, on raising the temperature of the specimen to 293 K, vigorous polymerisation took place; the final yield of the polymer reached 40%.

Under DIS conditions at 293 K and 77 K, 20 and 3% of the polymer were formed respectively; at 10 K the yield of the polymer was virtually zero. On raising the temperature, polymerisation did not occur apparently owing to the inadequate number of active centres, the possibility of the appearance of which was reduced probably as a consequence of the lack of high pressure gradients in the SW front. Degradation was not observed over the entire experimental range. The results obtained indicate a significant decrease of temperature in DIS compared with repeated shock compression.

The development of methods for the DIS of substances at low initial temperatures in experiments with preservation of the specimen created a possibility for the investigation of frozen gases or systems in which they are included. Tube designs were developed which permit the preservation of the above specimens after their dynamic isentropic compression to 50 GPa. Carbon dioxide, chlorine, water, a mixture of water and carbon dioxide, and a mixture of n-heptane and chlorine were investigated.[33] In order to observe the changes in the state of the substances at low temperatures, the RTL method was used. It was found that the RTL spectra of many substances subjected to compression differ from the initial spectra. For example, after the compression of $CO_2$, new peaks appear on the luminescence curve. The $C_7H_{16} + Cl_2$ mixture subjected to DIS loses its capacity for a rapid reaction in the region of the phase transition (at about 153 K), which is characteristic of an untreated mixture of these reactants.

The demonstration of the possibility of carrying out experiments with condensed gases under dynamic compression conditions with preservation of the specimens and of the

direct observation of their properties must be regarded as the principal result of studies of this kind carried out hitherto.

As research expands, an increasing number of processes which are favourably influenced by low-temperature dynamic compression are being discovered. For example, the low-temperature dynamic compression to 20 GPa of trioxan subjected to preliminary $\gamma$-irradiation induces a much greater increase in the yield of the polycrystalline polymer and of the number of chains that might have been produced by the simple summation of the compression and irradiation effects.[74] In order to increase the yield of the dense boron nitride phase, two-layer cylindrical tubes made of different materials have been used,[75] which led to an increase of the multiplicity of the shock compressions and to a decrease of the temperature developed in the specimen. When the molybdenum–iron pair was used, it was possible to attain a 70% yield on compression of boron nitride without additives. A layer of liquid hydrogen, which served simultaneously as the cooling agent, was used[76] as a light pressure transmitting substance. It was shown that, in the zone where DIS is active in copper, brass, and nickel specimens, a significant decrease of microhardness and of the density of traces of deformation was observed compared with the corresponding characteristics in the region of shock compression. The profiles of the compression waves in DIS are being investigated[77,78] and various schemes for the practical employment of layer systems have been proposed.[79]

We should like to draw attention to the following possibility which appears in connection with the development of methods for the attainment of DIS. In DIS the microshear deformations at the front and the temperatures developed are significantly reduced even by comparison with repeated shock compression, whereas the duration of action, the character of the decrease of pressure, and the degree of macroplastic deformations of the tubes with the specimen are virtually the same in both cases. DIS by itself does not as yet allow the separation of the role of microshear deformations and of the temperature factor, since a weakening of the influence of the former induces also a decrease of the temperature of the substance behind the front. However, preliminary heating of the substance under DIS conditions makes it possible to obtain $P-T$ conditions identical with those in the usual repeated shock compression and hence to isolate the influence of the SW front in a "pure form".

Two processes of different kinds, occurring on shock compression, have been investigated: the structural transformation of boron nitride into a dense diamond-like modification[80] and polymerisation of AA.[33] It has been shown that, when the experiments are carried out at low temperatures or at room temperature, the replacement of repeated SW compression by DIS prevents the structural transition in boron nitride. On the other hand, preliminary heating above 400 K is sufficient for the dense form of boron nitride to be produced both on DIS in 70% yield and on repeated shock compression. It has been shown in relation to the polymerisation of AA that the SW front is in fact responsible for the process, because preliminary heating of AA specimens up to the melting point did not increase the yield of the polymer, which remained an order of magnitude lower on DIS than on repeated shock compression.

### 3. The Attainment of Ultrahigh Pressures as a Result of the Head-on Collision of Shock Waves

The collision of planar SW and the attainment of ultrahigh pressures in specimens and their subsequent preservation for analysis have been achieved.[81] This became possible as a result of the construction of a symmetrical apparatus (Fig.7) in which two specimens of the test substance are subjected to two identical initial SW directed towards one another. We may note that modern explosive experimental technique makes it possible to synchronise with high accuracy the detonation of two identical explosive charges which accelerate identical impactors. An important requirement is the displacement of the test substance within the apparatus into the region not subjected to negative pressures which arise as a result of the interaction of the rarefaction counterwaves. When the layer 5 is made of a very dense material, for example, tungsten, it can promote a considerable increase of pressure in the reflected wave. If the shock adiabats for the materials and the velocities of the impactors are known, then the maximum pressure in the test substance can be estimated beforehand.

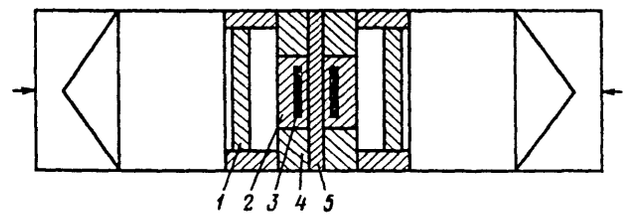



**Figure 7.** Schematic illustration of the experimental apparatus for the attainment of ultrahigh pressures on collision of planar shock waves: *1*) impactor (may be a multilayer impactor); *2*) preservation tube; *3*) test substance; *4*) protective ring; *5*) layer of a hard material.

The use of the method described for the treatment of substances by dynamic pressures makes it possible to increase greatly the maximum attainable pressures without complicating the existing systems and devices designed for the creation of high pressures in a one-sided impact. For example, at the velocities of the copper impactors usually employed, amounting to $\sim 2.0 \times 10^3$ and $2.5 \times 10^3$ m s$^{-1}$, pressures of ~50 and ~65 GPa respectively are developed in copper (or steel). The head-on collision of such impactors generates pressures of ~120 and ~170 GPa. The use of powerful explosives and greater charges makes it possible to increase the velocities of copper impactors to $\sim 3.5 \times 10^3$ m s$^{-1}$, whereupon pressures up to ~300 GPa can be achieved in a head-on collision.

Experiments have demonstrated[81] that the usual tubes with test substances withstand effectively pressures up to ~100 GPa. Above this pressure, changes in design are necessary in order to eliminate considerable macroplastic deformations. Experiments on the dynamic compression of polyethylene (PE) and polystyrene (PS) at pressures up to ~120 GPa have been carried out.[81] In order to achieve DIS, the head-on collision of two compound impactors made of perspex, aluminium, and copper has been used. Copper impactors, which determined the final pressure, had a velocity of $\sim 2 \times 10^3$ m s$^{-1}$. Analysis of the PE and PS specimens preserved after compression showed that they remained monolithic and semitransparent and were free from traces of degradation. A gel fraction was formed in PS in 100% yield owing to the formation of cross links, but, judging from the infrared spectrum, the decomposition of the benzene ring was not observed. We may note that

repeated shock compression of PS to 50 GPa leads to only partial formation of the gel fraction. It is known that $\gamma$-irradiation of polystyrene with a dose of 100 Mrad is necessary for the formation of 30% of the gel fraction.

The methods examined and the results show that both shock and isentropic compression waves or their various combinations can be used in head-on collisions. For example, a specimen subjected to preliminary DIS can be then acted upon by SW (Fig. 6*b*). The possibilities of this method have already been described.[33] In other words, it is now possible to achieve a controlled dynamic compression of specimens of different kinds and also to follow the variation of the state of the substance both in the course of compressing, by employing high-speed recording apparatus, and directly during the analysis of the preserved specimens.

## V. CHEMICAL SYNTHESES AND THE PREPARATION OF ULTRAHARD MATERIALS DIRECTLY IN THE DETONATION WAVE

Until recently dynamic methods for the preparation of ultrahard materials (UHM) such as diamonds and the dense modifications of boron nitride were based solely on the use of SW.[82] The initial materials are placed in flat or cylindrical preservation tubes which are penetrated by SW generated by a detonating explosive placed on the outside. Thus the detonation of explosives is used indirectly as a mixed external source of energy for the generation of SW. It has been shown in recent years that the detonation of charges made of a mixture of explosives and materials to be transformed (carbon or graphite-like boron nitride) entails the formation of UHM.[82] For this purpose, free mixed charges were detonated in stationary repeatedly reuseable hollow hermetically sealed containers, which made it possible to avoid the employment of disposable preservation tubes. It is significant that the detonation parameters (pressures up to 50 GPa and temperatures up to 6000 K) correspond to the region of the synthesis of UHM on static presses and overlap the part of the phase diagram which is difficult to attain, in which carbon and boron nitride exist in the liquid state.

The detonation synthesis[82] makes it possible to obtain diamond from various modifications of carbon, including amorphous modifications, with different fractional compositions. Depending on the experimental conditions, it is possible to synthesise the cubic modification or a mixture of the cubic and hexagonal modifications of diamond. Detonation diamond is a highly dispersed material with a high specific surface (20–150 $m^2\ g^{-1}$) and small coherent scattering regions (60–200 Å).

It has been shown that dense modifications of boron nitride can be obtained by detonation synthesis from both crystalline graphite-like and high-temperature boron nitride. Furthermore, depending on the detonation parameters of mixed charges, it is possible to achieve the specific synthesis of wurtzite-like or cubic modifications of boron nitride. As in the case of diamond, the particle size of the dense modifications of boron nitride is small—ranging from 0.05 to 5 μm, while the density is significantly lower than its theoretical value: 3.15–3.30 $g\ cm^{-3}$.

In considering the possible mechanisms of the formation of UHM, the hypothesis that carbon and boron nitride melt with subsequent crystallisation of the UHM from the melt appears to be of greatest interest. In particular, this hypothesis is supported by the synthesis of diamond from amorphous forms of carbon.

The question of the possibility of the synthesis of oxides, nitrides, and carbides directly in the detonation wave has been examined in a review.[33] The examples quoted indicate extensive new possibilities for the dynamic methods for acting on matter.

## VI. THE ROLE OF PLASTIC DEFORMATION IN DYNAMIC EXPERIMENTS AND THE POSSIBILITY OF COMPARING THE RESULTS OF DYNAMIC AND STATIC INFLUENCES

In discussing the questions concerning the role of plastic deformations, it is essential to differentiate two types of information obtained in the dynamic compression of matter. These include various characteristics recorded in the course of shock compression in the central region of the specimen, which is not yet affected by rarefaction waves, and the data obtained from them, for example, compressibility, electrical properties, etc. When the specimen is compressed by a planar shock wave, its central region is subjected to a one-dimensional compression without transverse deformations. The compression of a substance by powerful SW, whose amplitude greatly exceeds the yield point, makes it possible to neglect the effect associated with the hardness of solids. One can therefore assume that compression to a given pressure is the same as that which would have been achieved under a hydrostatic pressure of the same magnitude. This hypothesis is confirmed by the fact that in most cases the characteristics obtained by the shock compression methods merge smoothly, on extrapolation, with the characteristics obtained by static methods at lower pressures. For a number of substances, a satisfactory agreement has been observed as regards the onset of reactions in static and single shock compressions.[83,84] This applies, for example, to substances such as Fe, Bi, Si, Ge, P, I, Sb, Se, FeC, KCl, CdS, and GaAs.

It has been suggested that the martensite mechanism of the transformation predominates on compression by SW, whereas the change in the lattice is based on the cooperative displacement of many atoms over short distances. Such a transformation, which does not require an activation energy, can take place at very low temperatures at sonic rates of propagation, so that the particles of the new phase, with micron dimensions, are formed in the course of $10^{-7}$–$10^{-8}$ s. It has been suggested[84] that a complete identity of the phase transition pressures is possible for coordination crystals and layer structures with few defects. However, highly defective layer structures require higher pressures on compression by a SW than under static compression.

The specific features of shock compression are determined by the SW front in which the strongest microplastic deformations take place simultaneously with a sharp increase of the pressure and temperature. Despite the fact that the duration of the action of high pressure is only a fraction of a microsecond, i.e. is shorter by a factor of $10^7$ than in static compression, there is sufficient time for the occurrence of a wide variety of physicochemical processes in the test substances. The acceleration of processes in the SW has been compared by many investigators with the results obtained at high static pressures in combination with shear deformation (HP + SD)—see the relevant review.[85] However, the difficulty of comparing these two methods consists in the fact that under static conditions one investigates as a rule $P$–$T$ diagrams, while under dynamic conditions one obtains relatively simply and with a high accuracy $P$–$V$ diagrams. On the other hand, the temperature can be in the main estimated only by calculation subject to various simplifying assumptions. Furthermore, the pressure range in dynamic

experiments greatly exceeds that in static experiments. The question of the possibility of a comparison has been analysed in greatest detail in the review of Dremin and Breusov.[86]

Information about the influence of the rarefaction waves on chemical and phase transformations of a given substance in the course of shock compression is virtually lacking in the literature. Certain considerations concerning the role of rarefaction waves in the formation of active polymerisation centres and their contribution to the residual temperature have been published.[33]

When questions associated with the comparison of the changes in the properties of substances preserved in tubes after shock compression or after DIS are discussed, the situation is different. As already mentioned, in this case the specimen is acted upon by the full phase of the SW, including the rarefaction waves. Under these conditions, the specimen in the preservation tube inevitably undergoes major plastic deformations which depend on the compression conditions and the formulation of the experiment.

In considering the experiments in which specimens were compressed in cylindrical tubes, attention was drawn above to the complex pattern of the wave interactions and to the occurrence of the intense uncontrollable plastic deformations of the substance, leading to additional heating of the specimen. Nevertheless, it is sometimes possible to carry out a qualitative comparison of the results of static and dynamic experiments. We shall consider this in relation to the formation of polymeric molecules from unsaturated carboxylic acids—maleic (MA) and fumaric (FA), which are *cis*- and *trans*-isomers. Under the usual conditions, these acids do not polymerise owing to steric hindrance. However, it has been shown[87] that under HP + SD conditions at 6 GPa they undergo oligomerisation. The oligomers have a molecular weight of 700–800, which corresponded to a chain consisting of 6–7 molecules.

These objects behave differently on shock compression. Whereas both oligomers with a chain length of 5–7 units and polymeric products with a molecular weight (MW) of $3 \times 10^4$ (chain length of 250 units) are formed in MA on compression in flat and cylindrical tubes, in FA polymeric products are detected only under the conditions of enhanced deformations in the cylindrical tubes.

When special precautions are taken, the use of a planar compression scheme makes it possible to alter specifically and within wide limits the degree of radial macroplastic deformations of the specimens. Fig.5 illustrates the design of tubes in the usual formulation of the experiment (*a*) and in an experiment where the degree of deformation is specified beforehand (*d*), in which the specimen is capable of being deformed during the period of the operation of the high pressure ($\sim 10^{-5}$ s) and of filling the free volume in the tube. Such conditions were first used in the study of the influence of the degree of macroplastic deformations as a function of pressure on the polymerisation of acrylamide in a layered tube.[88] An increase of the degree of deformation of the specimens from 1 to 17% at the same pressure led to an appreciable increase of the number of polymer chains formed and of the yield of the polymer.

The scheme for the creation of specified macroplastic deformations has been used also in the study of the possible abiogenic syntheses of aminoacids in nature from nitrogen-containing organic compounds using as an example the reactions of the ammonium salts of unsaturated carboxylic acids under dynamic compression[89] and on their deformation under the conditions of a high static pressure up to 6 GPa.[90] The dynamic compression of the specimens was achieved in five different regimes. Shock compression, shock compression with a specified degree of deformation (up to 160%), DIS by the usual method, and DIS with a specified degree of deformation of the specimens were achieved in the planar arrangement, while in the cylindrical version the system was also subjected to shock compression. The pressure was varied from 5 to 11 GPa and the initial temperatures were varied from 77 to 300 K.

It has been shown[89,90] that, both in the HD + SD method and on dynamic compression, the ammonium salts of acrylic, methacrylic, crotonic, fumaric, and maleic acids can be converted into aminoacids. The yield of aminoacids on dynamic compression depends on the pressure, the initial temperature, and especially on the compression regime. The maximum yield has been attained in the presence of enhanced macroplastic deformations (Fig.5d) in planar compression under DIS conditions and in the cylindrical compression scheme.

It is to be hoped that the proposed schemes for compression with a specified degree of deformation will make it possible to compare quantitatively the results obtained in the HP + SD method and in different dynamic compression regimes and to discover the role of the SW front, plastic deformations, kinetic factors, etc. in various physicochemical processes.

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The technique of dynamic experiments in which provision is made for the preservation of the test specimens after compression in order to investigate the changes which they have undergone made it possible to extend the range of thermodynamic parameters compared with the traditional studies of the state of substances in the course of shock compression with subsequent breakdown of the specimen. Treatment of specimens in the pressure range 10–100 GPa and above and at temperatures up to $10^4$ K has become a realistic possibility. The useful volume of the specimens of the test substances is not limited at much higher pressures, in contrast to static apparatus.

The set of systems for the preservation of substances which have undergone dynamic (shock or isentropic) compression developed has made it possible to achieve various physicochemical transformations.

Methods permitting the attainment of controllable changes in the character of the dynamic compression and of the degree of deformation and also experiments at very low initial temperatures permitted in many instances the determination of the mechanism of the action of the SW and the role of its front. These experiments should promote the joint employment of the results of dynamic and static investigations, particularly in the HP + SD method. The possibilities of the dynamic method have not as yet been fully elucidated, as shown, for example, by the synthesis of ultrahard materials directly in the detonation wave.

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# Inorganic Chemistry of High Dynamic Pressures

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The causes and history of the appearance of a new field in the physical chemistry of high pressures, namely the chemistry of shock compression, are examined. Cases of phase transitions under the influence of high dynamic pressures which in principle cannot occur on static compression, namely transformations involving a decrease of density, are also described. Various types of chemical reactions, mainly syntheses, in condensed inorganic substances under the influence of shock waves are examined. Attention is concentrated on the mechanisms of chemical reactions and on the synthesis of new compounds and solid solutions, including those with atoms in unusual oxidation states. The prospects for the further development of the inorganic chemistry of shock compression are assessed.
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## I. INTRODUCTION

Together with variation of temperature, the nature of solvents, and the state of aggregation of the reactants, the high pressure technique has come to be used on an increasingly wide scale in recent years in synthetic methods of modern chemistry in order to influence specifically the structure and composition of the given substance. By varying the pressure, it is possible to influence various levels of the organisation of matter. It has been established experimentally that plastic deformation of the majority of materials is observed in the pressure range 1–10 kbar, polymorphic transformations take place in the range 10–100 kbar, while in the range 100–1000 kbar the outer electronic structure of atoms changes. Although the van der Waals, atomic, and electronic interactions can be separated only to a first approximation, it is evident that an increase of the level of pressures gives rise to new possibilities for influencing matter.

It is known that the technique employed in generating high static pressures suffers from two important limitations. Firstly, the pressure attained in presses is limited by the mechanical strength of the working material of the apparatus; record static pressures (1–2 Mbar) have now been obtained using diamond anvils. Secondly, an increase of pressure is accompanied by a decrease of the working space within the presses. As a result, in laboratory diamond presses the useful volume is now reckoned in microns and experiment makes it possible to obtain only new information about the given substance and not to synthesise materials with new properties.

The above limitations led to the need for a fundamentally new method of generating high pressures which would be free from the above disadvantages. Such an alternative procedure proved to be the dynamic methods for compressing matter with the aid of shock waves. It is noteworthy that the general theoretical questions of the physics of shock waves have been inadequately developed. The gas-dynamic principles of the theory of shock waves have been described in familiar monographs[1–3] and we shall therefore confine ourselves merely to a description of the principal terminology of this branch of physics.

Shock waves are formed as a result of the collision of molecules and particles travelling at an ultrasonic velocity with a stationary or moving barrier. The shock waves formed in the barrier are propagated at a rate $D$ and cause the migration of the bulk of the substance at a rate $u$. The dynamic pressure developed in the given body is

$$p=\rho_0 Du\ , \qquad (1)$$

where $\rho_0$ is the initial density of the compressed substance.

The energy source of shock waves may be provided by the detonation of explosives, an electric discharge, the work of the evaporation of solids on irradiation with a powerful light source, an electron beam, etc. The period of the increase of pressure from the normal value (1 atm) to the maximum value is $10^{-10}$–$10^{-12}$ s, the period of the high pressure is of the order of $10^{-6}$ s, and the period of the decrease of the pressure (relaxation) is $10^{-5}$–$10^{-6}$ s. The region in which the pressure increases is called the shock wave front and extends from tens to thousands of angstroms depending on the state of aggregation of the substance of the specimen.

Precisely because of the concentration of energy in space and time, it is possible to increase greatly the pressure by the dynamic method. However, the brevity of the duration of the dynamic pressure has posed new questions—is there sufficient time during such a brief period for the atoms in the structure of the solid to undergo a rearrangement and, even more so, is there sufficient time for a chemical reaction to occur in a mixture of the substances compressed by the shock wave. Only when these questions are resolved in a positive sense, will it be possible to claim that chemists have acquired a new instrument for influencing matter.

Evidently, the above problem can be solved only provided that the specimen subjected to the action of powerful shock waves is preserved (in a mechanical sense) so that is can be investigated by traditional physicochemical methods. Since the temperature also increases on shock compression, the study of the substance exposed to a shock wave would make it possible to compare its properties with the characteristics of the same substance heated to the corresponding temperatures at the normal pressure. If the results proved to be the same, then, from the chemical standpoint, the shock wave

is simply a means of heating the substance, but, if a difference is observed, then the new physical procedure has novel aspects. The solution of this problem, the protection of specimens against mechanical breakdown, and their careful physicochemical study, were the main topic investigated during the initial stage of the development of the chemistry of shock compression.

We shall consider briefly the sources of the appearance of this new field of study, namely the level of knowledge from which extensive experimental studies began in the 1960's in the field of the chemistry of shock compression. In 1938 to 1949 Michel-Levy and co-workers[4-6] described experiments in which the formation of silicates was noted on detonation of a mixture containing metal silicon oxides. In 1944, when two brass discs were exposed to a detonation pulse, they were found to be joined together (welded).[7] In 1948 Carrington and Gayler[8] described the change in the real structure of iron, duralumin, and silver after pulsed compression, namely an increase in the number of defects and in the strength of the metals was observed.

The next major step was taken in 1954 by Walsh,[9] who suggested, on the basis of the form of the shock adiabat for iron, the possibility of a phase transition under the conditions of dynamic compression. The study of the real structure of iron after its shock compression confirmed this hypothesis.[10,11] In 1956 Bancroft et al.[12] investigated experimentally the dynamic compressibility of iron and observed at 130 kbar a break on the curve relating the volume to pressure and detected ε-iron in the shock compression products, which indicated unambiguously the polymorphic transformation of iron in shock waves.

Non-metallic objects were first investigated in 1956 by Ryabinin,[13,14] who studied chemical compounds subjected to dynamic compression in cylindrical tubes; he observed the appearance of defects and processes involving the total or partial decomposition of organic and inorganic substances. In 1958 a technique for shock pressing, particularly in relation to aluminium and iron oxides, was described.[15] A marked distrotion of the structure, up to the complete conversion into the amorphous form (vitrification) of crystalline quartz was observed by De Carli and Jamieson.[16] Finally in 1961 the same workers[17] observed, after the shock compression of graphite (at $p \cong 300$ kbar), minute crystals of diamond in the specimen, in full agreement with the equation of state for carbon published by Leipunskii[18] in 1939.

In our view, the study of De Carli and Jamieson[17] completed the series of investigations which led to the establishment of the principal elements in the new scinetific discipline—the physical chemistry of shock compression. In the Soviet Union this was formally recognised at the Novosibirsk Scientific Centre of the Siberian Division of the USSR Academy of Sciences by the organisation of the Division of the Physical Chemistry of Pulsed Pressures. The results of the investigations in this Division have been described;[19] an analogous series of physicochemical laboratories have been established in Moscow at the Institute of Chemical Physics of the USSR Academy of Sciences. The combination of the physics of shock waves, the "preservation technique", and the chemistry of the solid state has in fact led to the attainment of very high values of thermodynamic parameters, made it possible to ensure the mechanical preservation of the product of the exposure of the given substance to explosion, and permitted the optimum selection of the objects of study.

An extensive literature on the chemistry of shock compression has already accumulated and it is virtually impossible to consider it in a single review. In the present article we shall therefore summarise the development of only the inorganic chemistry of high dynamic pressures and in our treatment we shall deal consistently with all the deeper levels of the structural changes in matter under the influence of shock waves and the corresponding molecular-physical and chemical consequences of these changes. This approach cannot naturally reflect all the studies on the problems considered. Additional literature may be found in other review articles.[20,21]

## II. THE CHANGE IN REAL STRUCTURE

When shock waves are propagated through a crystalline specimen, fragmentation and disorientation of the crystallites take place at the boundary between the compressed and unperturbed substance as a consequence of the steep pressure gradient. This results in an increase of the density of dislocations and of the microhardness of the specimen. This was first observed by Klein and co-workers[22-27] (in relation to MgO).

The present author investigated[28-31] single crystals of alkali metal halides in fluorite, preserved after a dynamic stress, and in a number of instances the dislocation densities and microhardness were determined for different orientations of the crystals. It was observed that, after dynamic compressions up to 60–80 kbar, the dislocation density in alkali metal halide specimens increases by 5–6 orders of magnitude. The increase of the density proved to be minimal for the <110> direction, while during annealing the decrease of the number of dislocations and of the microhardness was faster along the <111> direction. The latter factor can apparently be accounted for by the anisotropy of the plasticity of the crystals. The disorientation of the blocks in the single crystals subjected to shock compression which we investigated varied in the range from 40' to 3°.

The experimental surface dislocation densities ($10^{10}$–$10^{11}$ $cm^{-2}$ for alkali metal halides and $10^{12}$ $cm^{-2}$ for MgO) can be accounted for with the aid of the following estimates. The size of the crystal blocks [coherent scattering regions (CSR)] in single crystals subjected to shock compression is $\geq 100$ Å.[30,32] If it is supposed that dislocations constitute the boundaries of these blocks, then the maximum number of surface dislocations per $cm^3$ is ~$10^{18}$–$10^{19}$ and the dislocation density is therefore ~$10^{12}$–$10^{13}$ $cm^{-2}$. As a consequence of the residual heat, some of the dislocations disappear and the density is reduced by 1–2 orders of magnitude. Thus the residual dislocation density should not exceed $10^{11}$–$10^{12}$ $cm^{-2}$, as has in fact been observed experimentally.

In the study of dislocation structures by the method of etch figures, an interesting feature was observed[30]—the inheritance of the properties of the initial material by the substance subjected to shock compression. Thus, after shock compression, LiF, NaCl, and CsI crystals retain the initial dislocation structure, against the background of which new dislocation networks appear. On the other hand, in the case of KBr, which undergoes a phase transition under the conditions of the dynamic stresses employed, a new dislocation pattern was found after compression, which is apparently due to the breakdown of the initial structures as a consequence of the migration of atoms. It has been suggested[33] that a polymorphic transformation should altogether destroy the crystallinity of the given body, but experiment has shown that a single crystal can be preserved even after phase rearrangement.

At the same time, quartz[16] and silicate crystals undergo a complete or partial conversion into the amorphous form under the influence of shock waves. The latter phenomenon has been studied in greatest detail[34,35] by optical and X-ray

methods. It has been shown that sections (submicroscopic inclusions) of a disordered amorphous phase arise in the bulk of the crystals; as a result, the anisotropy of the properties of the shock-compressed crystal diminishes and its parameters approach those of isotropic bodies.

X-Ray studies of the dynamic compression of single crystals have shown that crystalline order is immediately established behind the shock wave front in LiF,[36–38,41,44,45] Al,[39,43] and BN[40,42] and that the shock compression at a high pressure is isotropic at the level of the unit cell. After the phase transition, the X-ray reflections for KCl[43] were appreciably weakened and broadened, which indicated the fragmentation of the blocks to dimensions of ~100 Å. After the shock compression of NaCl,[44] a monoaxial deformation was observed and the existence of crystalline order in the course of a microsecond behind the shock wave front was noted. The lines on the X-ray diffraction patterns for NaCl and KCl proved to be broader than for the initial single crystal and the intensity of the reflections was lower; however, the lines were more distinct than for a typical powder. The boradening of the lines can be accounted for by the fragmentation of the grains and the increase of the dislocation density. The reflections on the X-ray diffraction patterns of specimens of shock-compressed NaCl disappear 0.8 μs after the pressure peak as a consequence of the distortion of the crystal by plastic deformation.

Thus, according to X-ray diffraction data, the shock compression of single crystals at high pressures takes place isotropically, at moderate pressures deviations from the isotropic behaviour are observed, while at low pressure monoaxial compression takes place. In the region where a high pressure operates ordering of the material is observed and relaxation is accompanied by its deformation and disordering. This factor enabled American[36,40] and German[44] investigators to suggest that the fragmentation of the grains and in general the change in the real structure take place as a consequence of extensive stresses in the decompression wave and not at the front of the shock wave.

At the same time, the present authors' first experiments on the real structure of single crystals[28,30] showed that, with increase of the weight of the explosive charge, i.e. with increase of the smoothness of the decompression, and with decrease of the effects of the extensive stresses, the dislocation density either does not change or actually increases somewhat. Hence it follows that the shock wave front plays an important role in the formation of defects, while during decompression the material either becomes more defective owing to plastic deformations or less so as under the influence of temperature (see below).

Simultaneously with the study of single crystals, much attention has also been devoted to the investigation of the real structure of polycrystalaline materials subjected to the action of dynamic stresses. The pattern of the distribution of shock waves in powders is more complex than in single crystals, since in the former case the effects on the surfaces of crystalline grains are also manifested—repeated reflections, splits, contact fusion, surface evaporation, etc. Table 1 presents the minimal dimensions of the CSR of shock-compressed polycrystalline materials according to the present authors' data;[46] the substances are arranged in order of decreasing degree of dispersion of the material attained in a single step on shock compression.

The minimum CSR cannot be reduced by subjecting the same material to repeated shock compression. Thus single compression of $CaF_2$ and $BaF_2$ resulted in the appearance of anisotropic (in conformity with the different strengths in different directions) crystalline blocks whose size was 180–600 and 220–380 Å in the <110> and <111> directions respectively.[47] As a result of repeated compression, the crystallites became fragmented only along the major axes; the dimensions of the maximum axes of the ellipsoidal CSR in the $CdF_2$ and $BaF_2$ specimens diminished to 380 and 260 Å respectively, while the lengths of the minimum axes did not change on repeated compression. An analogous picture was obtained also in the shock compression of magnesium and aluminium oxides. This approach to isometric CSR corresponds to the enhancement of the isotropic nature of the properties on shock compression observed in relation to single crystal silicates (see above).

Table 1. Dimensions of the crystallites in shock-compressed powders.

| Substance | CSR, Å | Substance | CSR, Å |
|---|---|---|---|
| C, $TiO_2$ | 100 | $UO_2$ | 230 |
| $Al_2O_3$ | 130 | $Al_2SiO_5$ | 250 |
| BN, AlN, Mo | 150 | Ni, $LaB_6$ | 270 |
| LiF, MgO | 160 | Cu | 350 |
| $CdF_2$ | 180 | ZrC | 370 |
| $CaF_2$ | 190 | NaF | 440 |
| $BaF_2$ | 220 | | |

The results of the determination of the distribution of grain sizes in powders are also consistent with X-ray diffraction data for the degree of dispersion of polycrystalline materials: it has also been observed that large crystalline grains are fragmented more intensely than small ones.[48,49]

The above findings suggest that the "fragmenting effect" of shock waves has a definite limit (as if the crystalline powder were forced through the openings in a "sieve" of specific size). We shall consider the mechanism of the operation of this "sieve" and the factors which determine the size of the openings in it. If we turn back to the pattern in the propagation of a shock wave in a crystalline specimen, then it is easily seen that the crystals experience the maximum stresses (pressure gradient) only in the shock wave front, since ahead of the latter the unperturbed substance is present, while the region behind it contains the compressed substance. The depth of the front is usually estimated as equal to approximately ten unit cell parameters, i.e. ~100 Å.[50] Thus the minimum opening in the "sieve" is determined simply by the structure of the shock wave front. It has been shown[51] that, under the influence of shock waves, the crystalline grains in various types of steel assume a form close to an ellipsoid with the minor axis perpendicular to the shock wave front.

Generally speaking, the mechanism of the fragmentation of crystals can be various. If the size of the crystallites $l$ is much greater than the depth of the shock wave front $h$, the situation is favourable for the appearance of pronounced distortions (deformations) of the blocks, which promotes further (in the relaxation wave) cleavage of the crystal along the "weakened" directions. If the size $l$ is comparable to $h$, then deformations or even microsplits of the grain boundaries appear under the influence of the high pressure. For $l \leq h$, the high pressure region does not distort or fragment the crystal blocks.

Consequently the crystalline grains are deformed mainly during the compression or decompression of the substance and that, after the crystal has been exposed to the high

pressure zone, the defects acquired previously do not disappear. The mechanism of such memory is apparently associated with the disorientation of the crystallites caused by the intense vibrational movements in the shock wave front and observed from the asterism of the X-ray reflections from the preserved crystals.

In fact the contraction of the polycrystalline specimens in the high compression region can abolish micropores and cracks and can increase the apparent size of the grains, i.e. can improve the crystallinity of the material but cannot bring the disoriented crystallites into contact to form a single crystal. All the defects and distortions which had arisen in a crystal during the shock wave stress or which had been present in the initial material, therefore reappear after the decrease of pressure. One may expect that, as a result, microstresses are more likely to arise in large grains than in small crystallites and the dislocation density will correspondingly increase in direct proportion to the size of the CSR and not in inverse proportion, as always happens in the usual grinding of powders. An analogous picture of this type of unusual dependence of the concentration of microstresses on the size of crystallites has been observed in the study of the influence of radiation on crystals.[52] An analogy between the effects of shock waves and radiation has been observed also in other cases, as will be seen from further exposition. Annealing of defects induced by shock waves and radiation restores the real structure of the substance to the state of equilibrium.

Table 2. Dependence of the microstresses on the dimensions of crystallites.

| Substance | CSR, Å | $10^3\langle\varepsilon^3\rangle^{1/3}$ | Substance | CSR, Å | $10^3\langle\varepsilon^3\rangle^{1/3}$ |
|---|---|---|---|---|---|
| $CaF_2$ | 330 | 1.2 | $Al_2O_3$ | 810 | 3.3 |
| $CaF_2$ | 370 | 1.4 | $Al_2O_3$ | 1500 | 3.6 |
| $CdF_2$ | 180 | 1.6 | Mo | 145 | 1.8 |
| $CdF_2$ | 380 | 1.8 | Mo | 185 | 2.5 |
| $CdF_2$ | 650 | 1.9 | Mo | 265 | 3.4 |
| $Al_2O_3$ | 660 | 2.4 | | | |

Table 2 presents the results of the study of real structures for a series of shock compressed polycrystalline substances by the present author and his co-workers[47] (the size of the microstresses is $\langle\varepsilon^2\rangle^{3/2} = \Delta d/d$, where $d$ is the interplanar spacing). Examples of the equilibrium relations between $\langle\varepsilon^2\rangle^{1/2}$ and CSR are not quoted here owing to their trivial nature. Comparison of the products of shock compression extracted, for example, from different parts of the preservation tube and exhibiting different types of dependence of the microstresses on the size of the crystallites makes it possible to obtain additional information about the temperature field in the given tube.

The accumulation of microstresses within large grains leads to their splitting during relaxation. As a result of the decomposition of the crystals, the substance evolves the excess free energy. When the critical dislocation density is exceeded, the crystals undergo brittle breakdown. We shall consider this density subsequently in the description of processes involved in the shock pressing of powders.

The dispersion of particles and the appearance in the latter of considerable microstresses after shock compression leads to an increase of the free energy and therefore affects the molecular-physical properties of the substance. Thus, in recording heating curves, it was observed that endothermic effects (fusion of powders) are weaker, while exothermic effects (chemical combination of atoms) are more intense than for the same mixtures before exposure to dynamic action.[53] Data obtained from the determination of the energy stored after exposure to shock waves in relation to magnesium and aluminium oxides agree with this result.[49]

The activation of powders by treatment with shock waves is technologically important (see below). The study of the real structure of the powders proved useful in the investigation of the topography and characteristics of the strengthening of solids, in the determination of the mechanisms of phase transitions, and even in the solution of problems concerning the construction of preservation systems. The procedure followed nowadays in the study of the real structure on the basis of the analysis of the form of X-ray lines constitute an extremely important stage in the investigation of the processes involved in dynamic action on a substance and in the analysis of the results.

## III. THE CHANGE IN ATOMIC STRUCTURE

The change in the atomic structure of a substance in the course of a long period has been the main aim of high pressure physics (for example, the conversion of graphite into diamond). At the present time, the aims and possibilities of the technique of high dynamic pressures have expanded, but polymorphic transformations still constitute a very important field with which investigators are concerned.

In the first stage of the study of the physical chemistry of shock compression attention was concentrated on the very fact of the presence or absence of phase transitions and then on the stage involving the determination of the pressures of these transformations—the results of dynamic and static experiments began to be compared, and finally the time came to discover the characteristics of the polymorphic transformations in the course of dynamic stress. Accordingly, we shall divide all the dynamic phase transitions investigated into three groups: transitions whose parameters are close to those of static transitions; transitions differing in the character or properties of products; extremely specific phenomena manifested only in shock wave processes.

We shall consider initially a qualitative picture of the compression of a solid. This process is known to begin with the compaction of the substance at the macroscopic level: air is forced out of pores, cracks are healed, and vacancies and dislocations are abolished. Next begins the compaction process involving the shortening of interatomic distances, first within the framework of the initial structure, giving rise to isomorphic compression. With decrease of the distances, the structure of the substance departs to an increasing extent from the region of thermodynamic stability. Finally the time comes when the given substance with the initial structure can no longer exist under the new thermodynamic conditions and its structure undergoes an abrupt rearrangement, i.e. a first-order phase transition takes place. If the compression process continues then at the next level of pressures a new phase transition can occur, etc. The sequence of polymorphic transformations under pressure, leading to an increase of density, i.e. to the coordination of atoms, has been studied in greatest detail in relation to dioxides ($MO_2$): the quartz ($SiO_2$) structural type, which has the coordination number C.N. = 4, is followed, in terms of increasing density, by the $TiO_2$ structural type, which has C.N. = 6; then we have the $ZrO_2$ structural type (C.N. = 7), which is converted into the

$CaF_2$ structural type (C.N. = 8), and finally we have the $PbCl_2$ structural type (C.N. = 9).[54]

Thus there is a series of minima on the potential surface of the crystal corresponding to different packing densities of atoms in space.

Apart from the principal minima, there is a possibility of the presence of subsidiary additional minima on the potential curves in the region of the thermodynamic stability of the main structures. Under the conditions of static compression, where the stress and its relaxation take place comparatively slowly, it is not possible to detect these states. A sharp decrease of the dynamic pressure and temperature makes it possible to "quench" and preserve the compressed state of the substance (without altering the symmetry of the crystal), which was first observed by the present author.[55,56] We call this type of structural change an isomorphic transition. It is noteworthy that, generally speaking, isomorphic transitions have been known also in the physics of static pressures.[57] Thus the imposition of static pressures on lanthanide compounds entailed an increase of the oxidation state of the metal and the corresponding reduction of the unit cell parameters without alteration of their symmetry. However, in dynamic compression a decrease in cell size has been observed also for compounds of metals which do not have higher oxidation states (naturally together with the classical cases of isomorphic compression accompanied by a change in valence).

**Table 3.** The isomorphic decrease of unit cell parameters.

| Substance | C.N. | Unit cell parameters, Å | | $\Delta a$, Å |
|---|---|---|---|---|
| | | initial | after compression | |
| BN | 3 | 6.66 | 6.56 | 0.1000 |
| CuBr | 4 | 5.690 | 5.643 | 0.0470 |
| $MnCr_2O_4$ | 6 | 8.422 | 8.414 | 0.0080 |
| $CaF_2$ | 8 | 5.4620 | 5.4592 | 0.0028 |
| $CdF_2$ | 8 | 5.3839 | 5.3819 | 0.0020 |

Table 3 presents the results of the determination of the unit cell parameters of isomorphic decompressed polycrystalline materials.[55] Evidently the degree of isomorphic compression increases with the looseness of the structure, which is as a rule inversely proportional to the coordination number. It is of interest that the observed isomorphic transitions precede the usual phase transitions, i.e. constitute, as it were, a preparatory stage for the geometrical rearrangement of the crystal structure. At any rate, we have never been able to detect in the preserved substance changes in the unit cell parameters in the pressure ranges where polymorphic transformations of the test substances are not manifested. Analogous isomorphic changes in parameters were found later also by other investigators.[58,59]

Although the changes in the unit cell parameters are small, nevertheless they have a marked influence on the physical properties of substances. Thus the decrease of the unit cell parameter of fluorite was only 0.01% of the bond length, while the dielectric constant of the substance increased under these conditions from 7.1 to 7.9, i.e. by more than 10%. In the case of CuBr the dielectric constant of the initial specimen, which was 10.0, increased after isomorphic compression to 17.8, i.e. by 80%, while the unit cell parameter decreased by only 0.8%. Such a sharp increase in the polarisability of the crystals of isomorphically compressed substances is due to the overlap of the electron shells of the atoms approaching one another.

When the state of the system under conditions of increasing pressure corresponds to the principal minimum on the potential surface, the usual phase transition with a total change in the structure of the substance takes place. If the compressed body does not then have defects (or their number is small), then the transition pressures in the static and dynamic experiments are found to be very close (Table 4).

**Table 4.** The phase transition pressures.[60]

| Substance | Pressure, kbar | | Substance | Pressure, kbar | |
|---|---|---|---|---|---|
| | static | dynamic | | static | dynamic |
| Fe | 130 | 130 | Ge | 120 | 125 |
| P | 90 | 100 | GdS | 27 | 28 |
| Bi | 25 | 27 | KCl | 20 | 19 |
| I | 240 | 270 | Si | 115 | 130 |
| Sb | 85 | 88 | $CaF_2$ | 100 | 120 |
| Se | 130 | 150 | GaAs | 193 | 203 |

The observed difference between the phase transition pressures (in Table 4) is caused not only by the possible experimental errors, including the chemical and structural differences between the test materials, but also by the dynamic compression temperature factor. In fact, in static compression it is possible to influence independently the temperature of the compressed specimen, cooling or heating it to a specific temperature (unless otherwise stipulated, this means that the compression was carried out at room temperature). On the other hand, in shock compression the stressed substance is simultaneously heated and the "dynamic" transition compression is therefore found to be higher than the "static" value. If the dynamic and static compression of the test substance are carried out at the same temperature, one may expect even better agreement between the pressures of the phase transitions carried out by the different methods.

The substances listed in Table 4 have one common feature—it is impossible to generate in them a sufficiently high concentration of defects. By applying various influences, the densities of these substances can be reduced only slightly, at most by 10%, while the densities of graphite and boron nitride can be reduced by 50%, for example by creating structural defects. The cause of this difference is the homodesmic character of the structures and in many instances (for P, Bi, I, and KCl) also the high plasticity of the crystals, which promotes the rapid drift of dislocations during the deformation and baring of the specimen even at room temperature.

In many substances with a heterodesmic structure, in particular a structure of the layer type (graphite, boron nitride), the phase transformation pressure under the conditions of dynamic compression can greatly exceed the "static" value, when the initial material has a sufficiently high concentration of defects.[61,62] As will be shown below, at a very high concentration of defects the break in the

shock compressibility curve can be altogher absent[63,64] and the shock compression products do not contain the high-pressure phase.

The thermodynamic cause of the increase of the phase transition pressure in the dynamic compression of a defective crystal is then reduced density, which leads to an increase of the effective porosity of the specimen (at the atomic level) and hence to an increase of the shock compression temperature, which makes it essential to increase the pressure in the system. At a very high concentration of defects, i.e. for substances close to the amorphous state, the spreading of the phase transition boundary owing to the structural inhomogeneity of the specimen is observed, a classical example being provided by the softening temperatures of glasses.

Defects also influence the kinetics of the transformation. Evidently vacancies, dislocations, and disorientations of the blocks in the crystal structure lead to the breakdown of the coherence of the rearrangement and to the retardation of the transformation. In order to eliminate defects, it is necessary to perform work, which is executed under high pressure conditions by increasing the duration and intensity of the stress. Since on exposure to shock waves the duration of the dynamic pressure is limited, only the second procedure remains—one involving the increase of the pressure corresponding to the onset of the phase transition.

This effect obtains also in static compression. Thus in a study of the polymorphism of potassium and rubidium halides, we observed[65] that consecutive compression of the same specimen (accompanied by an increase of the concentration of defects) entails a constant growth of the pressure corresponding to the onset of the transformation, which can exceed the standard value almost by 100%. Thus, when the specimen is enriched in defects, the phase transition may not be observed at the standard pressure, for example, in the shock compression of certain kinds of graphite and boron nitride.[63,64]

It is noteworthy that the increase of the pressure of the onset of the transition is always accompanied by a decrease of the pressure of the end of the transformation, as a result of which the average phase transition pressure remains approximately constant. Thus, when the specimen is enriched in defects up to a certain critical value, the lower branch of the hysteresis loop reaches the normal pressure region. In other words, at the normal pressure it is possible to preserve the high pressure phase. This is in fact the reason for the existence over a specific period of structures of the CsCl type in alkali metal halides forced through draw plates at high pressures.[66]

Presumably, under the conditions of shock compression, where the increase and decrease of pressure take place over a very short time (i.e. the most favourable conditions are created for maximum hysteresis), the high-pressure phases are retained to an extent which is impossible under static conditions. This factor is extremely important for experiments with preservation of shock-compressed specimens, where it is possible to achieve not only the usual polymorphic transformations, which occur also under static compression, but also unusual transformations characteristic only of high dynamic pressures.

We shall begin the examination of the experimental results with the usual first-order phase transitions. The study of lanthanide and actinide compounds subjected to the action of explosion has occupied a significant place in Soviet research into the chemistry of shock compression. Thus in 1965 we carried out a physicochemical investigation of the products of the shock compression of the *C*-forms of lanthanide oxides and in 1966 evidence was obtained for the $C \rightarrow B$ transformations of all $Ln_2O_3$ for which such modifications had been unknown under normal conditions.[19] It is noteworthy that in 1964 the *B*-forms of a number of lanthanide oxides were obtained in static experiments,[67] but the physical properties of these substances were not investigated. In our communication[68] we therefore quoted the X-ray parameters, densities, refractive indices, and infrared spectra of *B*-$Ln_2O_3$ and also the temperatures at which these modifications are annealed (in the range 350–500 °C) with reformation of the *C*-form, which indicates unambiguously the physical nature of this transformation. The comparatively low annealing temperature of the *B*-forms necessitated special measures to reduce the influence of the thermal factor in dynamic compression: in order to achieve polymorphic transformations, cylindrical tubes with a central metallic rod were used.[68] Subsequently the transitions of lanthanide oxides from a *C*-type structure to the *B*-form were confirmed in other investigations.[69,70]

In 1966 phase transitions were observed in the compounds $MF_4$, where M = Ce, Th, or U, and were subsequently investigated in detail.[19,71–74] Whereas the initial tetrafluorides had a structure of the type of $ZrF_4$, after shock compression structures of the type of $LaF_3$ were obtained, where 25% of the sites in the cationic sublattice are vacant (for this reason, the formulae of the new modification should be more correctly written as $M_{0.75}F_3$). Refractometric studies confirmed the increase of the coordination number of the atoms in the crystal structures of these compounds under the influence of shock waves. The structure where together with the compaction of the substance atoms are "subtracted" from the metallic sublattice is also apparently formed as a consequence of the quenching of the shock-compressed substance. The absence of an analogous phase transition under static compression agrees with this hypothesis,[75] although the author[75] does not rule out the possibility that the required pressure may not have been attained in this instance. A phenomenon which is in essence analogous was subsequently observed in other studies[76,77] where the shock compression of $Nb_2O_5$ and $Ta_2O_5$ led to the formation of a structure of the $TiO_2$ type with a very slight change in composition.

Classical polymorphic transformations involving an increase of density as a result of the application of high dynamic pressures were achieved in our studies for lanthanide sulphides $Ln_2S_3$.[78] Like the oxides, the sulphides of light and heavy lanthanides differed in their structures and before dynamic experiments phase transformations involving an increase of density were achieved under the conditions of static compression.[79] Dynamic compression of terbium, dysprosium, holmium, erbium, and yttrium sulphides also led to a transition from the monoclinic form (of the type of $Ho_2S_3$) to a denser cubic form (of the type of $Th_3P_4$).

Transitions resulting from the shock compression of the hexagonal (quartz-like) $GeO_2$ also belong to classical polymorphic transformations involving an increase in the coordination numbers of the atoms.[80,81] It is known that under normal pressure $GeO_2$ exists in two forms—the low-temperature form of the type of rutile (C.N. = 6) and the high-temperature form of the type of quartz (C.N. = 4). At temperatures above 1000 °C a transformation of the $6 \rightarrow 4$ type takes place, while below 1000 °C there is a $4 \rightarrow 6$ transformation and static pressure does not exert a significant influence on the limits of the thermal transition.[82] Furthermore, in the absence of heating, solely under the influence of a moderate static pressure, the transformation of the $4 \rightarrow 6$ type in pure $GeO_2$ proceeds extremely slowly owing to the low rate of diffusion.[83] On the other hand, under the influence of dynamic pressures, the transition involving an

increase of the C.N. in $GeO_2$ proceeds very readily. If an intense shock wave is employed, then polymorphic transformations in the crystalline phase are accompanied by the formation of the yellow vitreous $GeO_2$. When the compression conditions were altered, a dense glass was obtained in which both four- and six-coordination of the germanium atom was observed by infrared spectroscopy. Such a rutile-like structure in vitreous germanium dioxide was obtained for the first time by ourselves.[81]

When the usual vitreous $GeO_2$ was exposed to an intense shock wave, not only the rutile phase but also a still denser (by 5%) crystalline modification was subsequently found.[84] It is of interest that the static compression of vitreous $GeO_2$ also entails the formation of a new, denser phase.[85] According to Ahrens,[86] the vitreous phase is the most convenient source of stishovite (for further details, see below).

As already stated, the vitrification of silicon dioxide under the influence of shock compression was first observed by De Carli and Jamieson.[16] The phase transformations in silicon dioxide involving an increase of density have been investigated in two studies;[87,88] the first study led to the detection of stishovite and the second revealed the presence of coesite. Subsequently this system was investigated by Dremin and Breusov.[89–91] We may also note a study[92] whose authors concluded that a phase transition of the 4 → 6 type in quartz occurs at such a high temperature that it involves the formation of a dense glass with the $SiO_6$ group in the first coordination sphere. In this connection we shall note the results of investigations of meteorites from craters in which both coesite and stishovite were discovered,[93,94] and dense forms have been frequently detected as inclusions in a mixture of crystalline and vitreous silicon dioxide.[95] This finding assisted us in selecting a natural method for the synthesis of dense forms of $SiO_2$, namely intense shock compression of quartz and subsequent separation of the products of the dynamic treatment with the aid of heavy liquids. Coesite and stishovite can be readily obtained by this procedure as a result of the shock compression of α-quartz.[96]

The question of the stabilisation of shock phase transitions is of fundamental importance but is still far from being solved. Even in those cases where it is possible to preserve the new phase after the explosion, there is no certainty that this is the precise phase formed under the conditions of high dynamic pressures. For example, a break at 330 kbar has been observed[97] on the compressibility curve for $TiO_2$ and the change in the volume of the specimen in the phase transition was by 21%. However, in the preserved specimen, the new modification having a distorted fluorite structure proved to be significantly less dense. The authors suggested that, at the instant when the substance was acted upon by the shock wave, a structure of the $PbCl_2$ type was formed and that the degree of coordination of the atoms and the density of the substance decreased during decompression; the dense modification decomposed under the influence of the residual heat. The rapid annealing of the dense modification at 550 °C has been noted.[98]

Various procedures are used to diminish the effect of annealing under the influence of residual heat. The most obvious method is to reduce the degree of filling of the tubes or one can even proceed to the shock compression of single crystals, which has been successfully demonstrated in two investigations.[58,99] The "chemical" procedure involving the wetting of the powder in the preservation tube with water, which by filling the pores displaces air and because of its higher heat capacity induces a sharp decrease of the residual temperature of the evolved heat, also proved extremely useful. The degree of decomposition of $PbO_2$ in the phase transition has been reduced in this way[100] and transitions known from static experiments for CdS and $CaCO_3$ were observed. After the shock compression of an aqueous suspension of HgO, a new (brown) modification of mercury(II) oxide was obtained,[101,102] differing appreciably in its properties from the known red and yellow forms. Despite the significant differences in the molecular-optical properties and in the density of the brown form of HgO, the X-ray characteristics of this phase proved to be virtually indistinguishable from those of the known modifications. The X-ray absorption spectrum and the $L_{III}$ absorption edge of the brown form has undergone a bathochromic shift.[103,104] On this basis, the authors[101,102] suggested the occurrence of local changes in the coordination of the oxygen atoms in the brown modification although the large difference between the atomic numbers of mercury and oxygen precluded the detection of an inclusion of the new phase by X-ray methods. A neutron diffraction study of the brown modification of HgO yielded some evidence in support of this hypothesis.[105]

As already stated above, in layer structures such as those of graphite and boron nitride, the transition to the diamond structure in specimens with a high content of defects under the influence of shock waves is hindered ("smeared") or is even altogether absent. Shock wave experiments with graphite have been carried out since 1961 (see above and also Trueb[106] and Gust[107]), while boron nitride was first subjected to shock compression and was preserved for subsequent study as late at 1965 in our laboratory.[108]

The shock compression with the aid of a cylindrical scheme of pyrolytic low-density BN led only to a slight increase of the density of the specimen, although small transparent crystals with a density of 2.5–2.6 g $cm^{-3}$ were observed along the axis of the cylindrical tube; their X-ray diffraction pattern contains, among others, lines due to the wurtzite modification of BN: 2.20 (m.), 2.08 (m.), 1.95 (m.), 1.54 (w.), 1.26 (v.w.), and 1.17 (v.w.) Å. The presence of reflections from other interplanar spacings did not allow us to claim that the new phase (we called it the "E-phase") contains a diamond-like modification as a component, although the lines quoted above undoubtedly indicate a geometrical relationship between the E-phase and the dense forms of boron nitride. In 1976 this modification was produced by Japanese investigators in the shock compression of BN (using a planar scheme) to 600 kbar, the initial materials being subjected to two (in succession) dynamic compressions.[109] This factor is extremely significant, since, after the first shock compression, a multiplicity of defects arise in the material and the structure of the latter approaches that of the pyrolytic state, i.e. conditions very close to those in our experiments are realised. The E-phase has also been obtained[110] in a pulsed discharge between boron rods in a nitrogen atmosphere, being detected after a short exposure to these conditions, whereas an increase of the duration of the exposure (of the number of pulses) led to the formation of the classical diamond modification. Hence it was concluded that the formation of the E-phase is the first stage in the transformation of the graphite structure into the diamond structure. Finally, the E-phase has been recently obtained when the graphite-like boron nitride was subjected to laser irradiation and an increase of the duration or the intensity of the irradiation again led to the formation of the wurtzite-like modification of BN.[111]

The simplest explanation of the nature of the E-phase would involve the hypothesis that a mixture or a solid solution (for example, the type of block isomorphism) of the graphite and diamond phases of BN is formed. However, the identity of the properties of the E-phase specimens obtained by different procedures and also the change of

only its concentration and not of its characteristics when the applied dose of the given influence is changed indicate the individuality of the product. Unfortunately, owing to the low quality of the crystals, only the unit cell parameters could be determined: $a = 7.2$, $b = 8.1$, and $c = 18.9$ Å.[112]

Later Kurdyumov and Pilyankevich[113] obtained a polycrystalline carbon with similar properties, which they regard as an analogue of the E-phase. Although the above phase was called simply the dense modification (of the diamond type) in a well known review,[114] we believe it to be useful to differentiate it as an intermediate structure in which the graphite networks may be connected by diamond bridges in a specific sequence (see Noda and Inagaki[115]).

The diamond forms of BN have been obtained by the shock method[116,117] and it has been shown[117] that the yield of the dense forms increases in parallel with the increase of the density (i.e. of the degree of perfection of the crystals) of the initial graphite-like boron nitride. At the same time we demonstrated independently[80] that the structural perfection of the hexagonal BN is essential for the success of the phase transition. Next we obtained dense forms of BN by the shock compression of a fairly perfect initial material.[118] The crystallographic aspect of the transition of the hexagonal boron nitride to the tetragonal or cubic modifications has been examined in detail.[119] The mechanism of the phase transformation of the graphite-like modification to the diamond modification was later investigated[113] from the standpoint of the real structure of the initial and shock-treated boron nitride.

In conclusion of the description of the polymorphic transformations on shock compression, we shall consider certain unusual phase transitions, which cannot occur on static compression of the test substance. We have in mind the phase transitions involving a decrease of density. Generally speaking, the annealing of the dense modifications under the influence of the residual heat, which was already discussed above, can be regarded as the formal outcome of the dynamic compression of the given body. However, for substances which undergo phase transformations with compaction of the structure after heating under normal pressure (AgI, PbO, MnS, $Ln_2O_3$, etc.), the temperature and even more so a high pressure can no longer promote a decrease of density. In other words, the dense modifications of substances of this class cannot be converted into the loose modifications for any kind of change in the thermodynamic parameters. The study of precisely such substances in our laboratory, starting from 1965, revealed phase transitions involving a decrease of density, i.e. the exposure to shock waves led to a change from irreversible to reversible transitions. The first review of the literature devoted to this topic was written by the present author[19] and more detailed information can be found in other communications.[60,112]

After the discovery of phase transitions involving a decrease of density on shock compression, analogous transformations were achieved in experiments involving the irradiation of substances,[120] in the comminution of crystals in a ball mill,[121] and on static compression with shear.[122] In all these processes the generation of a large number of defects entails partial or total conversion of the substance into the amorphous form, which leads to the activation of the powder and the creation of conditions for the appearance and rapid growth of the nuclei of a new phase which is stable under the given thermodynamic conditions†. Thus, under the influence of shock waves, the initial structure breaks down and the residual heat induces the crystallisation of a new phase, which is initially less dense, while further heating leads to the formation of the densest phase.

According to the model developed above, the physical cause of the decrease of density is the decrease of the coordination number of the atoms as the crystalline grains are fragmented. Since the fragmentation of crystals entails an increase of the fraction of surface atoms, which have smaller coordination numbers than in the bulk of the crystal, comminution is always accompanied by a decrease of the static (effective) coordination number of the atoms. Estimates have shown that, when account is taken of the decrease of the coordination numbers owing to the formation of vacancies and dislocations, fragmentation to a size of 50–100 Å is sufficient to reduce the effective coordination number by 1–2. In this case the energy of the comminution (which appears as an increase of surface energy) is comparable to the heat of the phase transition.

It is of interest to analyse the polymorphic transformations in steels from the standpoint described. It is known that the heating of iron is accompanied by the $\alpha \rightarrow \gamma$ (or $\beta \rightarrow \gamma$) transition involving an increase of density. The reverse transition takes place under the influence of various kinds of deformations, including those induced by the dynamic compression.[123] It is significant that the polymorphism of pure iron is of the reverse character and only after the introduction of carbon or other "hard" additives does the phase transition under the influence of any kinds of deforming forces become possible. Leaving to one side the possible (slight) change in the composition of steels in the polymorphic transformation, the role of alloying additives can be naturally accounted for by a decrease of the rate of elimination of defects as a consequence of the decrease of the plasticity of the material. As soon as this rate becomes lower than the rate of deformation of the material, conditions are immediately generated for the accumulation of defects, i.e. for the conversion of the substance into an amorphous form.

In the first stages the unusual phase transformations were investigated mainly by optical methods and also by measuring the density and by recording heating curves. In all cases the loose modifications were converted after annealing into dense modifications with an exothermic effect, which indicated the absence of a change in the chemical composition on exposure to shock waves. Table 6 presents the structures and densities $\rho$ of certain lanthanide compounds which have undergone a phase transition with decrease of density under the influence of dynamic pressures.

Apart from polymorphic transformations, it was possible to obtain as a result of exposure to shock waves modifications which differed from the initial forms only in the size but not the symmetry of the unit cell.[55] Such transformations were called isomorphic by analogy with the physics of static pressures, where appreciable changes in the parameters without a change in the structural type have been observed in relation to lanthanide metals and their compounds.[57] Whereas such transformations have been induced under static conditions by a change in the oxidation state of the lanthanides, with the aid of the dynamic method the isomorphic transitions have been achieved for compounds of a wide variety of metals, including those which have only one oxidation state. Furthermore, phases involving an increase in the unit cell parameters, caused by a weakening of the chemical bonds as a result of the dynamic pressure, have been obtained on exposure to shock waves.

If account is taken of the fact that, with increase of the density, isomorphic compression precedes the polymorphic transformation, the isomorphic expansion of the parameters

†In the case of α-spodumene, the intermediate amorphous phase was detected experimentally.[124]

can be naturally correlated with the phase transitions involving a decrease of density which have just been discussed. Table 5 presents the X-ray diffraction data for the isomorphically expanded materials. The average differences of the unit cell parameters ($\Delta a$) are quoted for anisotropic substances.

Table 5. The increase of unit cell parameters in isomorphic transitions.

| Substance | $\Delta a$, Å | Refs. |
|---|---|---|
| $SiO_2$ | 0.013 | [125] |
| $SiO_2$ | 0.067 | [125] |
| Ni | 0.04 | [126] |
| $NdF_3$ | 0.027 | [127] |

Table 6. The properties of polymorphic modifications.

| Substance | Initial phase | | After shock compression | |
|---|---|---|---|---|
| | structure | $\rho$, g cm$^{-3}$ | structure | $\rho$, g cm$^{-3}$ |
| $SmF_2$ | $LaF_3$ type | 6.93 | $YF_3$ type | 6.64 |
| $HoF_2$ | $LaF_3$ type | 7.83 | $YF_3$ type | 7.64 |
| $Tm_2S_3$ | $Ho_2S_3$ type | 6.27 | new phase | 6.06 |
| $Nd_2S_3$ | A-form | 7.42 | C-form | 6.29 |

In conclusion of this Section, we shall attempt to answer the question how the phase transitions occur under shock compression. One should apparently consider separately two types of transformations—those in which there is a possibility of a coherent shift of all the lattice atoms over a short distance (the so-called martensite transitions) and transformations which require the preliminary rupture of the initial structure. Since the changes in bond lengths associated with the usual changes in coordination numbers are within the limits of the vibration amplitudes, the martensite transition can be readily accounted for in terms of a vibrational mechanism, i.e. it should occur at the velocity of sound. The presence of an amorphous phase as an intermediate state is essential for transitions of the second type. In this state the atoms are probably extremely mobile, since they are not linked to their neighbours and resemble free radicals. Thermodynamically, the state corresponds to the disappearance of the potential barrier between the two modifications.

The conversion into the amorphous form gives rise to the possibility of the formation of a phase with a reduced density. Furthermore, in the amorphous (vitreous) initial material the phase transition should take place more readily. Indeed, in many instances the phase traosformation of glasses has been observed at lower pressures than in the corresponding single crystals.[84,85,86,128] It is shown below that the reconstructive phase transitions and the active intermediate state involved in them play an important role also for chemical processes.

## IV. CHEMICAL REACTIONS

Processes involving the synthesis and decomposition of chemical compounds have been investigated from the very beginning of the development of the new scientific discipline; furthermore, the very name, shock compression chemistry, presupposes the preservation of the specimen exposed to shock waves for further study.

The chemical investigations have been carried out in terms of two aspects—in order to solve problems of practical importance and to obtain specific substances, on the one hand, and in order to develop the method itself and to elucidate the mechanism and the characteristics of the chemical reactions under the conditions of shock compression, on the other.

We shall consider initially the second question, which is in essence fundamental for the entire chemical component of the dynamic method. The most important task is to determine the period of the reaction, i.e. to determine the possibility of the completion of the reaction under the conditions of a high pressure during $10^{-6}$–$10^{-5}$ s.

There is as yet no evidence that the compounds produced under the conditions of shock compression and preserved for further experiments were obtained in the high pressure zones; this can be inferred only from indirect features. However, our present day knowledge about the processes occurring on shock compression of powders permits the conclusion that the character of the chemical processes under these conditions is non-trivial.

A specific feature of the chemical interaction under shock compression is that, under the influence of the shock wave, the crystalline grains are fragmented and a multiplicity of structural defects, namely vacancies, dislocations, and atoms with altered oxidation states, are generated in the particles; the particles of the mixture components interpenetrate one another during migration behind the shock wave front (owing to the differences between the mass velocities of the components), are deformed, and are pressed into a monolithic form. After the establishment of a uniform pressure in a mixture of fairly small particles, the components of the shock-compressed specimens can be compressed in different ways (owing to the differences between the mechanical properties of the reactants) and hence can be heated in different ways. Estimates have shown[129] that the difference between the temperatures of the "hot" and "cold" points in a shock-compressed mixture reaches hundereds of degrees.

If one takes into account further the fact that the plastic deformations occurring on pressing the powders will also cause unequal heating of different mixture components and even different parts of the grains,[130] then it becomes evident that the additional effect may amount to a further several hundred degrees.[131] Thus the overall temperature difference between adjoining sections of the mixture can exceed 1000° and can lead to diffusion and even the evaporation of individual particles. This factor constitutes a fundamental difference between the heating of the reaction mixture by the shock wave and the homogeneous heating of the same composition in the usual furnaces.

Finally, the rapid migration of the shock wave front promotes the rapid propagation of the chemical reaction zone. For highly exothermic reactions, this process can be analogous to high-speed combustion or even detonation.

The characteristic features of the shock compression method gave rise to the hope that unusual results might be obtained. Certain conclusions from the investigations made can now be reached.

The first shock syntheses of substances from the elements were performed by Japanese workers. Thus in 1963 Horiguchi and Nomura[132] reported the synthesis of TiC (see also Ref.133). The same investigators subsequently obtained WC[134] and $Al_4C_3$.[135] Suzuki et al.[136] synthesised TiC, ZrC, and SiC; all these substances are of interest for the preparation of ultrahard materials. Simultaneously with the solution of practical problems, studies were made of the characteristics and mechanism of the reactions. Thus Horiguchi and Nomura[133] suggested that the shock wave leads to te mechanochemical activation of the reactants and compresses the mixture in which "hot" points, initiating the chemical reactions, are distributed. The subsequent development of the chemical process takes place as a consequence of the liberation of heat at the active centres. Suzuki et al.[136] noted the dependence of the thermodynamic parameters in the cylindrical preservation tube on the location of the specimen and showed that the reactions proceed with the maximum intensity in the axial region of the cylinder.

Adadurov et al.[137] synthesised by the shock compression method a number of silicides from the elements—FeSi, $FeSi_2$, and $V_3Si$. Otto and co-workers[138,139] obtained the intermetallic compounds $Nb_3Sn$ and $Al_3Nb$, which are of interest for the study of superconductivity. These workers used copper tubes to improve (as a result of the high plasticity of copper) the compression of the materials; in addition, they employed evacuated preservation tubes before the dynamic experiment. According to these workers, the mechanism of the formation of the intermetallic compounds involves the shock fusion of one of the components, for example, tin, and the dissolution of the other component in it.

The shock compression of Nb–Ge, Nb–Sn, and Nb–Pb mixtures has been described.[140] The syntheses of $Nb_3Si$ and $Ta_3Si$ have been reported.[141,142] Savitskii et al.[143] carried out the shock compression of 3Nb + Y (Y = Si, Ge, Sn, Pb, or In) mixtures and observed that the synthesis occurred only in the axial region of the cylindrical tube.

Elementary syntheses in our laboratory have been carried out in order to investigate mainly the characteristic features of the duration of the shock synthesis of transition metal chalcogenides. In the synthesis of chromium chalcogenides the influence of fine shock dispersion of the powders on the endothermic effects of the fusion process and the exothermic effects of the chemical reactions was observed.[53] Modifications of chromium monochalcogenides with reduced density and with retention of the type of crystal structure were obtained in the same study (see above).

Batsanov et al.[144] determined the temperature of the Sn + S reaction mixture 0.05–0.1 s after dynamic compression, which proved to be 1100 °C. The residual temperature in the case of SnS, synthesised beforehand by the usual method and then shock-compressed under the same conditions, was only 130 °C. Bearing in mind that the residual temperature during the measurement (after 0.05–0.1 s) only decrease, one can conclude that the reactons have been completed by this time. The same paper describes an interesting instance of the influence of particle size on the degree of reaction and even on the direction of the reaction in shock synthesis. An equimolar Sn + S mixture consisted of powders with particle sizes ranging from 0.06 to 0.4 mm; all the experiments were performed with the tube filled to the same extent and with all other conditions kept the same. It was found that, in the range 0.06–0.2 mm, the yield of SnS increased with decrease of the particle size. The grain diameter increased to 0.2–0.4 mm and the degree of conversion of sulphur rose from 45 to 80%. This was caused by the change in the composition of the product: the reaction product proved to be $SnS_2$. This unusual fact can be explained by taking into account the thermal instability of tin disulphide at temperatures above 600 °C. Since the amount of heat evolved increases with increase of the surface energy of the powder (see the synthesis of chromium chalcogenides described above[53]), there exists a critical particle size above which $SnS_2$ is stable.

The interaction of the chalcogens sputtered in the form of thin films on the surfaces of plates, under the influence of shock waves directed at right angles to the plane of the plate, has also been studied.[145] The chemical compound is formed as a result of the mutual diffusion of the tin and chalcogen atoms. An increase in the duration of the shock pulse entails the growth of the diffusion zones: for example, for a 3.2 km $s^{-1}$ pulse, the thickness of a tin sulphide layer is 1 μm whereas for a 7.8 km $s^{-1}$ pulse it increases to 3 μm. It is significant that treatment with shock waves promotes also the usual thermal diffusion. Thus, when specimens compressed by a 3.2 km $s^{-1}$ pulse for 50 h are heated, the diffusion zone is 9 μm thick, whereas for the non-compressed specimens the diffusion zone is only 4 μm thick in such heat treatment.

The characteristic features of the diffusion of atoms in a solid subjected to shock compression have been investigated.[146] The authors showed that, in the pulsed compression of a metal, the rate of diffusion can be actually higher than in its melt. It is also of interest that the rate of diffusion was higher in the dense γ-iron lattice (of the face-centred type) than in the less dense α-iron (of the body-centred type), which the authors explained by the sharp increase of the number of point defects in the case of the face-centred lattice. The acceleration of the movement of atoms in the shock-compressed materials has been explained[147] by the decrease of the activation energy for diffusion owing to the decrease in size of the particles and the corresponding decrease of their melting point.

A sharp increase of the rate of the chemical reaction of the elements can be achieved by employing the method of detonation synthesis.[148,149] The absence of metallic tubes leads to close contact between the energy carrier and the material being treated, as a result of which very high temperatures and pressures are generated by this method. Calorimetric and X-ray studies have shown that, during a period of ~$10^{-5}$ s, the synthesis of zinc chalcogenides takes place quantitatively.[149]

Compounds in known structural forms were obtained in all the studies enumerated above. On the other hand, compounds in new crystalline forms were produced in the synthesis of lanthanide sesquichalcogenides, for example, those of holmium and erbium.[78] The shock synthesis of neodymium and samarium monochalcogenides[150] yielded a series of new solid solutions with an intermediate (between 2 and 3) oxidation state of the metal.

Reactions of the type metal + the oxide form of the compound have also been achieved under the conditions of shock compression. The first publication on this topic concerned the reactwon Cu + $CuBr_2$ → 2CuBr[55] with reduction of the unit cell parameters (Table 3). A decrease of the oxidation state of titanium via the reaction Ti + $TiO_2$ → 2TiO has been achieved by Ruchkin et al.,[151] while a decrease of the oxidation state of indium in $InF_3$ in the interaction of the latter with metallic indium has been carried out by Batsanov et al.[152] The interaction of lanthanide trifluorides with various lanthanides, which yielded both pure[153] and mixed[154] fluorite

phases, has been studied in detail. The doubly charged state of the lanthanide in these compounds has bee confirmed by optical and magnetic data.[155,156] The oxidation state of the metal could be reduced only in copper[157] and chromium[158] oxides and in the latter case a chromium(II) compound was detected by means of a special system in which two reactants were separated in space within the tube and only one was subjected to shock compression, as a result of which one reactant was swept onto the other by the Mach wave. The reaction mixture is very rapidly cooled in such a system, which promotes the quenching of the metastable compound. We recently synthesised neodymium monoxide by the reaction $Nd + Nd_2O_3 \rightarrow 3NdO$, the mixture of components being initially repeatedly subjected to the action of shock waves and then heated at 600 °C for 100 h;[159] this compound has a structure of the NaCl type, but its unit cell parameter proved to be 5.096 Å, i.e. greater than that for NdO obtained on static compression of the same mixture,[160] which suggests the formation in our case of a compound of neodymium in an oxidation state less than 3.

Apart from the processes involving a decrease of the oxidation state of the metal by some other metal in a free state, the reactions involving the reduction of oxides by other elements have been investigated. Thus the shock interaction of $Ln_2O_3$ with B yielded[69] $LnB_6$. The authors[69] believe that the reaction proceeds after the completion of the shock compression due to the residual heat in the preservation tube. The shock reduction of $SnO_2$ by carbon, silicon, and aluminium, accompanied by the mechanochemical treatment of the mixtures in ball mills, has been described.[161] The importance of the area of the contact surface and of the local temperature ("hot" spots) has been noted.

The shock reactions of metals with Teflon, which proceed in accordance with one of the two equations

$$M + (CF_2)_n \rightarrow MF_x + C,$$
$$M + (CF_2)_n \rightarrow MF_y + MC$$

have been investigated recently.[162] Fluorite phases have been obtained with the aid of these reactions for scandium and yttrium. The reaction of metals with water led to the synthesis of a number of metal oxides, hydroxides, and peroxides.[163,164] The aim of these studies was to elucidate the question of the possible completion of the chemical reaction during the period of shock compression. These experiments were based on the following reasoning. Since water at high pressures has the properties of an acid, the shock compression of the metal + water mixture can lead to the displacement of hydrogen, provided that the metal is electrochemically more active than water (or when the water remains chemically "inert" if the metal is more passive). It is important that the reaction should proceed only in the high pressure zone where water has acid properties. Experiment fully confirmed these hypotheses, but the question of the residual temperature in such a suspension remains open, since in the case of heating to a high temperature there is a possibility of simple pyrolytic decomposition of water by the metal.

We shall now proceed to the description of the results of studies of the reactions of oxides and compounds with one another. In 1963 the shock compression of an equimolar mixture of zinc and iron oxides yielded zinc ferrite[165] (see also Adadurov et al.[166]), while in 1966 zinc orthosilicate was synthesised from a mixture of zinc oxide and silica.[167]

Lanthanide mono- and tri-hydroxides, LnOOH and $Ln(OH)_3$ were synthesised in 1967 by the reaction of lanthanide sesquioxides with water.[168] Tubes with a reduced strength, which remained integral during the experiment if all the water combined with the oxide and were ruptured if water was taken in excess, were used in the above study. Thus the stoichiometry of the chemical reaction can be inferred even from the mechanical behaviour of the tubes. Dremin and Breusov[89] described the syntheses of silicates, double fluorides, and garnets. Subsequently barium titanate was synthesised by the shock compression of a mixture of $BaCO_3$ and $TiO_2$.[169] Data on the shock synthesis of magnesium and calcium metasilicates as a result of the compression of mixtures of the corresponding oxides and silica have been published.[170]

Lanthanide oxides or chalcogen fluorides have been obtained in our laboratory[171] as a result of the dynamic compression of mixtures of fluorides with lanthanide oxides or chalcogenides. It has been shown for samarium oxide fluorides that, in the presence of a slight excess of the fluoride in the initial mixture, a tetragonal oxide fluoride is produced, whereas in the presence of an excess of the oxide the product is the rhombohedral modification, the cubic SmOF phase being formed only on compression of a stoichiometric mixture. As a result of the movement of masses in the course of shock compression, for example, in a cylindrical tube, there is a possibility of the local breakdown of the reaction stoichiometry as a consequence of the distillation of the mixture components, i.e. the "polymorphic transformation" of complex compounds becomes possible. The $PbO + TiO_2$, $PbO + ZrO_2$, and $2PbO + TiO_2 + ZrO_2$ interactions have been investigated under the conditions of shock compression.[172] The stoichiometry of lead zirconate-titanate (LZT), which is an extremely important piezoceramic material, is infringed in its usual thermal synthesis owing to the unequal volatilities of the components. On the other hand, in the shock compression of the initial mixture of oxides, synthesis, pressing, and shaping of the compound produced take place simultaneously.

Complex formation in accordance with the equations $2KX + PtY_2 \rightarrow K_2PtX_2Y_2$, where X and Y are halogens of different kinds, has been described.[173] We believe this reaction to be promising from the standpoint of the synthesis of inner sphere complexes of coexisting ligands, which cannot be combined [in the same coordination shell] by the usual methods of synthesis. We synthesised by the reaction $SmO + TiO_2 \rightarrow SmTiO_3$ a compound in which there is a definite competition between the Sm(II) and Ti(IV) oxidation states.[129] Evidently analogous compounds can be obtained also by the reaction of titanium monoxide with lanthanide sesquioxides. It is entirely likely that a kind of valence isomerism can occur in this instance. We obtained compounds of the type $Ln_2O_3.MO_2$ and $Ln_2O_3.2MO_2$ by the reaction of lanthanide sesquioxides with $TiO_2$, $ZrO_2$, and $HfO_2$ [59,174] and investigated the dependence of their structure on composition. We recently studied the shock reaction occurring via the mechanism $Ln_2O_3 + Ln + 3/2I_2 \rightarrow 3LnOI$, the Ce, Gd, Ho, and Lu compounds having been obtained and investigated for the first time.

In conclusion of this Section, we shall consider the formation of substitutional solid solutions as a result of shock compression. The feature of the majority of substitutional solid solutions is that their densities are lower than those of the initial mixtures and is of methodological interest. The formation of stable solutions should therefore be caused by the temperature factor and, conversely, phase transitions or other structural changes in the solid solutions formed should take place under the influence of pressure. Indeed the synthesis of KCl–KBr solid solutions yielded[80] a substance with an increased density and the annealing of the product was accompanied by a decrease of density with the simultaneous evolution of heat (exothermic effect on the thermogram).[80] The shock compression of the RbCl–CsCl mixture

leads to the formation of solid solutions with a structure of the NaCl type, but their density again proved to be higher than the standard values.[175] It is significant that the composition of the solid solution did not depend on the component ratio in the initial mixture: the shock compression of a wide variety of compositions yielded a solid solution of the same composition.

The corresponding solid solutions were synthesised for the first time from $NH_4X$–$CsX$ mixtures by dynamic compression of the latter.[176,177] Solid solutionsof the $NH_4X$–$KX$ and $NH_4Br$–$NH_4I$ systems have also been obtained by the dynamic method, their compressibility increasing with the atomic number of the halogen.[178] A change in the intensity of the shock wave entails a change in the compositions of the solid solutions formed, which is characteristic of the chemistry of berthollides. Finally, shock compression of the KCl–CsCl mixture led to a decrease of the phase transformation temperature of CsCl from 469° to 305 °C, while the X-ray diffraction pattern of the mixture remained unaltered. A detailed study showed that the solid solution formed in this system remains in the X-ray-amorphous state at room temperature.[179]

Solid solutions of another type have been investigated in a series of studies. Thus Gryaznov et al.[180] investigated the saturation of iron by carbon under the influence of pressure pulses and showed that at 425 kbar carbon penetrates to a depth of 0.05 mm as a result of dissolution in a layer of melt on the surface and subsequent crystallisation. Kozorezov et al.[181] observed a considerable miscibility (greater by a factor of 7 than in the usual thermal synthesis) of tungsten and iron. Adadurov et al.[76] obtained a continuous series of solid solutions with compositions ranging from $Nb_2O_5$ to $NbO_2$ on the basis of the rutile structure. Such solid solutions were formed only for high intensities of the shock waves where the specimens were known to be in a fused state. A solution of gallium in copper with a concentration greatly exceeding the "thermal" value has been obtained by shock compression.[182] Finally, the ZnS + Se shock interaction led to the formation of a continuous series of ZnS–ZnSe solid solutions which have the sphalerite structure in the presence of ZnS contents from 0 to 50% and the wurtzite structure for higher ZnS contents.[183]

In conclusion of the description of shock syntheses, we shall now turn to the question of the duration of the chemical reactions. The usual objection against the possibility of the occurrence of reactions during such short periods arises from the relatively low rate of diffusion in solids, especially under high pressure conditions. However, experiments carried out in the authors laboratory, involving the measurements of the electrical conductivities of powders under pressure, have shown that the conductivity of ionic polycrystalline substances is fairly high under these conditions and does not increase with increase of pressure but increases until the attainment of the monolithic state. Furthermore, it increases sharply at the instant of the phase transformation of the chemical compound.[184] We believe the latter factor to be extremely important because it has been suggested[195] that the chemical reaction can take place during the period of high dynamic pressure, provided that at least one of the reactants undergoes a reconstructive phase transition under the given thermodynamic conditions. A direct experimental test of this hypothesis by investigating the phase transformations in the reacting systems is of interest.

Apart from syntheses under conditions of high dynamic pressures, studies have also been made of chemical decomposition reactions of substances and these had begun earlier than the synthetic experiments. Thus the appearance of metallic sodium as a result of the shock compression of NaCl has been noted.[14] Subsequently Nicholls et al.[186] observed a disproportionation under dynamic pressure into iron and lead oxides.

Batsanov et al.[187] undertook a systematic study of the possibility of the shock decomposition of complex oxygen compounds. A thermodynamic criterion was established, namely the enthalpy of formation of the compound above which the crystal structure is improved under the influence of a specific shock influence, while below it the substance decomposes.

The shock decomposition of alkali metal bromates and nitrates has been described.[188] In the former case an analogy has been observed between shock and radiation decompositions, while for nitrates the process is more complex. The formation of defects as a consequence of the action of an explosion on nitrates has been studied in detail in the present authors' laboratory and a definite analogy has been observed between the formation of shock and radiation defects.[19,189] Symons[190] studied by EPR the formation of radicals when binary oxides and sulphides and complex oxygen compounds are exposed to shock waves; a correlation with radiation defects (produced by $\gamma$- and $n$-irradiation) was not observed. An analogous study has been carried out by Nelson and Hartley.[191]

Lapshin et al.[192] investigated the chemical properties of $K_2S_2O_8$ subjected to dynamic compression and observed that the compression leads to the formation of the same paramagnetic centres as those produced during irradiation.

The decomposition of sillimanite into $Al_2O_3$ and $SiO_2$ has been observed.[193] Here an interesting result is the isolation of stishovite when intense shock waves are applied. This justifies the hypothesis that the compound decomposes under the conditions of high pressure.

It has been shown[194] that the CO and $CH_4$ shock adiabats can be described satisfactorily only if it is assumed that these molecules decompose at high pressures (in excess of 200 kbar) into diamond particles and gaseous $O_2$, $CO_2$, $H_2$, $CH_n$, and $C_2H_2$ molecules. We may note that the decomposition of $CO_2$ into diamond and $O_2$ has been observed at high pressures under the conditions of the static compression of $CO_2$.[195] Hence it follows that finely dispersed diamond can be obtained by the dynamic compression of hydrocarbons and carbonates.

Together with the usual decomposition of compounds as a consequence of shock compression, shock structure-breaking in substances exposed beforehand to hard radiation has been investigated.[192,196,197] Thus $K_2S_2O_8$ powder has been subjected to the influence of detonation[192] after its preliminary treatment with $\gamma$-radiation (from a $^{60}Co$ source). The $F$ centres were retained in the test substance after the shock compression, although the absorption spectrum changed appreciably compared with the substance which was simply irradiated. After the irradiation of alkali metal halide crystals and also $CaF_2$, $SiO_2$, and $(NH_4)_2S_2O_8$, the appearance of colloidal intralattice metal was observed.[196] Single crystal and polycrystalline NaCl specimens have been studied in greatest detail,[197] the intensity of irradiation and of the dynamic compression being varied within fairly wide limits. It has been established that the formation of a colloidal metal is characteristic of the single crystals, the size of the colloidal particles varying in parallel with the degree of distortion of the specimens; the $F$ centres are retained in the polycrystalline specimens. The latter fact is apparently caused by the higher rate of diffusion of atoms and the higher temperature in the shock compression of powders

compared with single crystals, which leads to the decomposition of colloidal particles on relaxation with formation of *F* centres. It is significant that the concentration of free sodium in the shock-compressed NaCl specimens proved to be higher than that of the *F* centres, which is probably caused by the additional injection of electrons in the course of the shock compression from the material of the preservation tube and from the impurities in the initial specimen. One should note further that the *F* centres in shock-compressed materials are unstable at room temperature—crystals can be decolorised by natural light in the course of several minutes or even seconds.

The first stage of any decomposition is accompanied by a decrease of the oxidation state of the metal owing to the dissociation of chemical bonds. The increase of the magnetic susceptibility of zinc sulphide on shock compression as a consequence of the Zn(II) → Zn(I) transition has been observed by Nomura and Tobisawa.[198] In 1967 the present author and his co-workers studied the Ti(IV) → Ti(III) transition[199] and then the Eu(III) → Eu(II) transition.[200,201] The change in the oxidation state of other lanthanides on shock compression was dealt with above.

The practical application of the shock method for the generation of structural defects, in particular the decrease of the oxidation state of the metal, involves the modification of catalysts by exposure to shock waves. Thus the influence of dynamic compression on the catalytic properties of transition metal oxides has been studied;[199] shock treatment led to an increase of the catalytic activities of ZnO, $TiO_2$, and $BaTiO_3$ by 2–3 orders of magnitude. This result was confirmed in another study.[202] We established that the increase of the catalytic activity of $TiO_2$ and other titanium compounds took place as a result of the formation of electronic defects, especially $Ti^{3+}$ centres. The shock compression has been used[203] to activate pyrites catalysts used in the liquefaction of coals. It has been shown[204] that, after the shock-wave treatment of $CaF_2$, which catalyses the dehydration and dehydrogenation of isopropyl alcohol, the temperature of the onset of the reaction diminished and the selectivity of the catalyst action increased. Increase of selectivity carried by dynamic influence has now been observed also for other catalysts.

Finally, we shall indicate yet another, analytical aspect of the shock compression chemistry. Since the substance treated is enclosed in a strong metallic tube and, generally speaking, there should be no loss of material in the course of the dynamic experiment, there is no need for the usual chemical analysis. The physical methods for the determination of the phase composition and the possible structural changes play an analytical role in this instance. However, the compressed substance may be contaminated by the material of the walls of the tube, which has been investigated.[205,206] It has been found that, when the substance is contaminated by iron in a cylindrical tube, the bulk of the impurities enter the compressed substance from the lower stopper at the centre of which a crater is usually formed as a consequence of the effect of the reflected shock wave.[206] The overall concentration of the impurities is correlated with the packing density of the powder before the experiment, the parameters of the shock wave entering the substance, and the presence or absence of phase transformations involving a change in the volume and compressibility of the given body.[207]

Thus spectroscopic analysis of a shock-compressed substance can serve as an indication of the physicochemical transformations which have occurred as a result of dynamic compression (including reversible transformations which cannot be observed in the preserved specimen).

## V. CONCLUSION

The new method whereby the composition and structure of a given substance can be actively influenced, namely shock compression, has immediately found extensive practical application. The fundamental studies and technical applications developed in parallel. Below we shall consider briefly the practical aspects.

We shall begin with the physical and mechanical manifestations of the changes in the real structure. The hardness of the material increases as a result of the fragmentation of the crystalline grains and the increase of the dislocation density under the influence of the dynamic compression, which has already been dealt with at the beginning of the review. Naturally the increase of hardness and hence in the strength of metals is of practical importance. The first review devoted to the metallurgical effect of shock waves is that of Appleton.[208] Subsequently monographs were devoted to this topic.[209–211]

The technical problems of the dynamic strengthening of metals are extremely varied and even a simple list of the results obtained would occupy far too much space. New data concerning different mechanisms of the thermal and shock strengthening of metals, which may lead to new prospects in this field of materials science, are noteworthy (see also Bekrenev and Naumov[212]).

The second major field in which the shock wave techniques are used is that of the pressing of powders. The advantages of the dynamic method compared with static pressing consists in the easier attainment of high pressures and the absence of limitations as regards the size of the treated articles. Several international conferences have been devoted to the application of dynamic pressures in the pressing of powders[213–215] and such pressures have also been considered at the All-Union Symposia on Pulsed Pressures.[216–221] In addition, shock pressing has been described in the above reviews[208,209] and in the original articles by foreign[48,49] and Soviet[222–224] workers.

At the same time, dynamic pressing suffers from serious limitations at the present time due to the specific features of the shock compression itself. We have in mind the phenomenon of "overpressing", which leads to the saturation of specimens by cracks and pores or even its fragmentation into small pieces. This phenomenon is due to the fact that the dynamic compression of the crystal increases the dislocation density of the latter and under certain experimental conditions the concentration of the defects can exceed the critical value for the given substance, after which the crystalline grain disintegrates into smaller particles. In order to prevent disintegration, one either heats the specimen between dynamic treatments in order to increase its plasticity or the maximum plastic deformation of the material is ensured.

The most important practical application of polymorphic transformations under the influence of dynamic pressures is the shock synthesis of diamond and borazone [boron nitride]. The main task here is the rapid removal of heat during (or after) decompression, since diamond and borazone are annealed to the graphite modification at $T \geq 1000$ °C. It is difficult to solve this problem, which has led to the following paradoxical situation: transformations of the graphite → diamond type take place quantitatively in the shock wave, but in the decompressed system the concentration of diamond is only several per cent. Numerous methods and patents have been devoted to the development of various procedures for the solution of this problem.

The application of synthetic methods involves in practice mainly the pulsed welding of metals, which leads to the formation (in the region of the join) of intermetallic compounds, including those which are not obtained in the traditional methods of synthesis. The pulsed welding of metals has found applications in various branches of industry for the large-scale manufacture of bimetallic plates and coatings for tubes and the flat surfaces of machines and mechanisms.[210,225] At the present time the manufacture of welded and strengthened constructions in our country has reached a rate of 100 tonnes annually and shows a tendency to increase.

The methods for the shock synthesis and modification of materials with the aid of a dynamic treatment have also found practical applications in a new branch of science and engineering—the synthesis of superconductors. Apart from the studies quoted above,[138–143] the newest investigations should be mentioned.[226–231] Dynamic experiments make it possible to include in this vigorously developing field methodological features such as high-speed deformation, rapid thermal quenching, and instantaneous increase and relaxation of pressure. In many instances these procedures can be used in technology.

Apart from the direct applications of the dynamic pressure techniques, the latter are used also for the preliminary treatment of materials in the usual technology—for the activation of powders or sintering, pressing, catalytic processes, etc.

Thus we have outlined the most general limits to the applications of the chemistry of shock compression. As regards the prospects for the employment of this method, the unusual nature of the temperature pattern of shock compression, deformation, electrical phenomena, and the enormous pressure gradients create a unique set of physical influences on matter. By varying the energy carriers, the duration of the pulse, the density, and the temperature of the ambient medium and by the joint or consecutive operation of various factors, it is possible to widen significantly the horizons in the application of the shock-wave techniques in chemistry. At the very beginning of the development of shock wave chemistry, its prospects seemed to be limitless; however, in the present author's view, even now the peak in the development of this field has not been passed.

We may note certain problems which have not found a practical solution. This concerns in the first place the synthesis of high pressure phases. Hitherto it has not been possible to obtain such phases chemically; the reason is that the reaction of solids takes place over period $\geq 10^{-6}$ s, i.e. when the high pressure has ceased to operate. The rate-limiting stage is naturally diffusion processes. However, if special measures are taken and the mixture components are comminuted to give a particle size of 0.1–1 μm, then the diffusion time is reduced by 1–2 orders of magnitude and there is sufficient time for the reaction to occur in the high pressure zone. By varying the sizes of the particles of individual components, it is possible, in principle, to "involve" wholly the various parts of the reaction in the chemical process. The successive employment of various pulsed influences—self-perpetuating high-temperature synthesis, electric discharge, shock waves, and radiation can be used for the same purpose. Additional possibilities arise in the inorganic synthesis of high pressure phases under the conditions of the technical application of ultrafast quenching (detonation synthesis "into space") or following the instantaneous imposition of a static pressure after shock compression (for example, in hermetically sealed tubes with water or other gas evolving substance).

The problem of the synthesis of complex and organometallic compounds by-passing the liquid phase appears to be extremely promising. At the present time many substances (with covalent bonds) cannot be directly involved in a chemical process, since they do not dissolve in the known solvents without decomposition and cannot be congruently fused (for example, NaH, $PtCl_2$, $CaC_2$, $CrO_3$, etc.). The chemical interaction under the conditions of shock wave compression in strong containers makes it possible to insert directly into the initial matrix additional atoms and molecules and to obtain new clathrate compounds (for example, silicates with neutral metal atoms incorporated in their vacancies) or complexes with unusual combinations of ligands [for example, $PtF_2Br_2$, $LnF_2I$, $K_2Ni(CN)_2Cl_2$, etc.]. The problem of the polymerisation of inorganic gases, which, as it now appears, can be solved on the basis of solid solutions or clathrate compounds, is also of interest.

These are the nearest prospects for the inorganic shock-wave chemistry, but, as this science develops, new even more interesting tasks may arise.

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# Diffraction Methods for the Investigation of the Electron Density and Dynamics of Crystal Lattices

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Precision diffraction methods for the investigation of the electron density, electrostatic potential, and dynamics of crystal lattices are described. Data concerning the fine details of the chemical bonds in compounds of various classes obtained with their aid are discussed. The forms in which the data on the distribution of electron density and electrostatic potential in crystals can be represented and interpreted are examined.
The bibliography includes 96 references.

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## I. INTRODUCTION

Two approaches to the description of the structures of molecules and crystals have arisen hitherto. The first of these, namely the quantum-chemical approach, reduces to seeking (in terms of a particular type of approximation) the solution to the Schrödinger equation and their chemical interpretation constitutes an exceptionally difficult problem. In the other, crystal-chemical approach, the structure of the substance is described on the basis of a simple geometrical model and the concepts of the effective charges and radii of atoms.

The two approaches have now come together to some extent owing to factors dictated by practical chemical problems. Qualitatively, the new level of these problems required a fairly rigorous description of the structure and detailed properties of crystals with a complex structure of chemical bonds. Such a description has been achieved by introducing the function $\rho(\mathbf{r})$ characterising the total electron density in the molecule or crystal. This function contains an appreciable proportion of the chemical information about the system, can be related to chemical concepts, can be visualised by graphical representation, and finally its values can be measured directly by X-ray diffraction. The last factor is of fundamental importance because, instead of abstract parameters, determined by wave functions, it makes it possible to describe the electronic structure of the substance with the aid of the experimental function $\rho(\mathbf{r})$.

Together with a brief description of the modern methods for the interpretation of diffraction data and the estimation of their accuracy, the aim of the present review is to demonstrate for a series of examples in what way the results obtained with the aid of precision X-ray measurements can be interpreted in terms of the language of quantum chemistry and crystal chemistry. It is particularly important that the data obtained by this method concern complex chemical compounds which are not susceptible to modern quantum-chemical computational methods.

The use of diffraction methods normally reduces to the determination of the coordinates and parameters of the thermal vibrations of atoms in the crystal lattice. However, by virtue of the significant increase in accuracy of structural analysis as a result of the wide-scale introduction of automatic diffractometers and the development of methods for the accurate interpretation of experimental data, detailed investigation of charge distribution and potential near the equilibrium positions of the atoms in crystals has become possible in recent years. The application of the neutron diffraction method in addition to X-ray data has significantly expanded the range of information obtained.

The qualitative imporvement of the apparatus for the diffraction methods has entailed a change in all the stages of the experiment and of the treatment of the results of measurements. We therefore thought it useful to describe concisely all the stages of the accurate measurement and interpretation of diffraction data. The expansion of experimental possibilities has sharply increased the number of studies based on diffraction methods. They have been devoted to the experimental refinement of the traditional ideas of structural chemistry and the theoretical interpretation of the data obtained. These questions, together with the description of the principles of the precision X-ray and neutron diffraction methods and the analysis of the accuracy of the results, the methods of their representation, and their comparison with data derived by quantum-chemical calculations, are examined in this review. The review does not deal with questions of the determination of spin and momentum densities by diffraction methods in molecules and crystals, which have been considered in detail in a collected volume.[1]

## II. EXPERIMENTAL STUDY OF THE DISTRIBUTION OF ELECTRON DENSITY

In terms of the adiabatic approximation,[2] it is possible to separate with adequate accuracy the movements of electrons and nuclei and to examine the electron subsystem for the nuclear configuration fixed by the thermal equilibrium positions. The structure and properties of the $N$-electron subsystem in the ground state are then described by the many-electron wave function $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)$, which depends on the three-dimensional coordinates and spins of all the electrons. This function can be found as the solution of the Schrödinger equation on the basis of the variational principle. This mathematically cumbersome procedure yields results which depend on the level of the approximations adopted and on the quality of the basis functions used.

For this reason, it is exceptionally difficult to obtain the complete wave function $\Psi$ which reproduces correctly all the properties of the many-electron system;[3] furthermore, the practical determination of such characteristics from $\Psi$ is fairly difficult. However, it is possible to use for the description of the majority of the physicochemical properties of molecules and crystals a one-electron density distribution function $\rho(\mathbf{r})$ with a simpler structure, the function depending solely on the three-dimensional coordinates of the point at which the charge density is to be determined. This function is related to $\Psi$ by the expression[2]

$$\rho(\mathbf{r}) = N \int \ldots \int \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \cdot \Psi^*(\mathbf{x}_1, \ldots, \mathbf{x}_N)\, d\mathbf{x}_2 \ldots d\mathbf{x}_N d\mathbf{s}_1, \qquad (1)$$

where $\mathbf{x}_i = \mathbf{r}_i \mathbf{s}_i$, $\mathbf{r}_i$ being the three-dimensional coordinates, $\mathbf{s}_i$ the spin coordinates of the $i$th electron, and $N$ the number of electrons in the system.

The theoretical interpretation of the function $\rho$ is significantly simpler than that of the wave function $\Psi$ and Eqn.(1) makes it possible to determine it.

The wave function $\Psi$ (with its numerical characteristics) can be calculated with the aid of one of the approximate versions of the solution of the Shcrödinger equation, for example, by the self-consistent field method in terms of the Hartree–Fock approximation, the configuration interaction method, and also the methods based on the band theory of solids. However, the problem of the correct description of the electron density distribution at all points in the test system is very difficult and such description has been achieved (with an error of approximately 0.1 $e\text{Å}^{-3}$) only for simple 2–6 atom molecules.[4,5] For more complex many-electron systems and especially for crystals, the realistically attainable accuracy of the theoretical calculations of electron density is to within approximately 0.3 $e\text{Å}^{-3}$, which is clearly inadequate for the solution of many chemical problems.

On the other hand, the function $\rho$ can be measured experimentally because elastic (Bragg) X-ray scattering by the crystal entails the interaction of the radiation with the electrons and the signal contains information about their distributions. Having measured the intensities of the X-ray reflections for various atomic planes with the *hkl* indices, it is possible to obtain the time-average electron density function† at any point with the coordinates $xyz$ in a unit cell having the volume $V$ (Vainshtein[6]):

$$\rho(\mathbf{r}) \equiv \rho(xyz) = \frac{1}{V} \sum_{hkl} F(hkl) \exp[-2\pi i(hx + ky + lz)] \qquad (2)$$

where $F(hkl)$ is the structural amplitude related to the reflection intensity measured in the X-ray diffraction experiment. Thus Eqn.(2) makes it possible to determine directly the electron density distribution in the crystal (Fig.1). The accuracy of the determination of $\rho$ depends on a number of factors and will be examined in detail below. Here we shall only note that in many instances the error can be only 0.02 $e\text{Å}^{-3}$.

The classical X-ray diffraction analysis of structure is based on the hypothesis that the maxima in the function $\rho$ correspond to the centres of gravity in the electron densities of the atoms; approximate values of these maxima can be found by special methods.[6] The coordinates of the atoms and the parameters of their anisotropic vibrations are then refined by the method of least squares based on minimising the functional

$$\Phi = \sum_{hkl} [F(hkl) - F_{\text{calc}}(hkl)]^2. \qquad (3)$$

The model of the structure to be refined is specified by the expression for the structural amplitude:

$$F_{\text{calc}}(hkl) = \sum_{n=1}^{m} f_n W_n(hkl) \exp[2\pi i(hx + ky + lz)],$$

where the atomic amplitude $f_n$ describes the scattering capacity of the $n$th atom with the coordinates $x_n$, $y_n$, and $z_n$ and the temperature multiplier $W_n$ takes into account the thermal parameters.

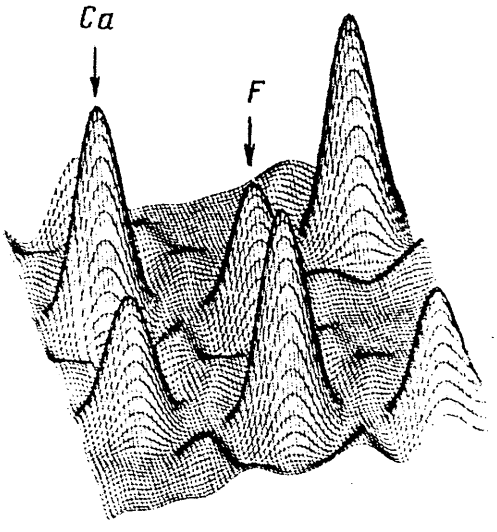



Figure 1. The map of the total electron density in the $CaF_2$ crystals; the maxima of the $\rho$ function correspond to the positions of the atoms.

The atomic amplitude $f_n$ is related by the Fourier transformation to the function of the static electron density of the atom. For an atom in the crystal, this function is never known accurately; to a first approximation, it is assumed that a crystal made up of spherically symmetrical atoms constitutes a satisfactory *a priori* model. This made it possible to describe and tabulate the values of $f$ for all atoms on the basis of the calculation of their spherically symmetrical electron densities by quantum-chemical methods; these $f$ curves are in fact normally used in practice.[7] The errors of their calculation are less than 0.5% (somewhat more for heavy atoms). However, one should note that the above error is not a criterion of the suitability of the spherical atom model for the refinement by the method of least squares. In fact, the modification of the atomic electron density through chemical interaction disturbs the spherical symmetry of the atom and leads to a dependence of the atomic amplitude on the direction of scattering of X-rays. The structural parameters found within the framework of the traditional approach can therefore contain errors associated with this factor.

†The averaging arises because the measurement takes place over a period of time.

In order to take into account the thermal movement of the crystals, one uses the approximation according to which the electron density $\rho$ "smeared" by the atomic vibrations is represented by the convolution of the theoretical static density and the distribution function $t(\mathbf{R})$ for the positions of the centres of gravity of the vibrating atoms $\mathbf{R}$.[8] For an individual atom, this can be formulated as follows:

$$\rho_n(\mathbf{r}) = \int \rho_n(\mathbf{r}, \mathbf{R})\, t_n(\mathbf{R})\, d\mathbf{R}. \quad (5)$$

The specific form of the function $t_n$ depends on the characteristics of the crystal field potential near the point of thermal equilibrium of the atom. In early studies, this potential was assumed to be harmonic and the function was represented by a three-dimensional Gaussian distribution function. However, in a real case the atomic vibrations are anharmonic and the anharmonicity parameters can be determined experimentally, which is done by introducing additional terms into the $t_n$ refined by the method of least squares.[8] An example of such a description is provided by the cumulative expansion of this function when the temperature multiplier assumes the form[6]

$$W_n = \overline{\exp}\left[-\sum_{ij}\beta^{ij}h_ih_k - \sum_{ijk}\gamma^{ijk}h_ih_jh_k + \sum_{ijkl}\delta^{ijkl}h_ih_jh_kh_l + \ldots\right], \quad (6)$$

where $\beta^{ij}$, $\gamma^{ijk}$, and $\delta^{ijkl}$ are the elements of the tensors describing the harmonic and anharmonic (third- and fourth-order) thermal vibrations of the atoms and the $h$'s are the Miller indices. Other expansions of the functions $t_n$ can also be encountered.[8]

A relation of type (2) can be obtained likewise for the distribution of nuclear density; in this case the structural amplitudes $f(hkl)$ are measured in a neutron diffraction experiment and the maxima of the density function correspond to the centres of gravity of the ellipsoids of the thermal vibrations of the nuclei. Owing to the small dimensions of the nuclei, the neutron scattering by the atom is spherically symmetrical. The amplitude of the coherent scattering of neutrons $b_n$ is determined by the properties of the given nucleus and, in contrast to the atomic amplitude $f_n$, is independent of both the magnitude and direction of the scattering vector, i.e. $b_n = \text{const}$.[9]

In terms of the adiabatic approximation, the parameters of the thermal vibrations of the atomic nuclei and of their electron shells are identical. In terms of this approximation, one can assume that the information obtained by the X-ray and neutron diffraction methods (taking into account their specific features—see below) is identical. However, one should note that at the present time the data produced by accurate diffraction experiments show that in certain cases the use of the adiabatic approximation is inadmissible; for example, highly delocalised valence electrons and conductivity electrons do not obey this approximation. On the other hand, if this approximation is adopted, then certain inaccuracies, mentioned above, in the determination of the structural parameters from X-ray data owing to the non-spherical nature of the electron density of the atoms can be eliminated in the subsequent analysis of the electron distribution. The analogous parameters obtained from neutron diffraction measurements can be used instead of the X-ray parameters.

The joint application of various diffraction methods can be generally speaking extremely useful. For example, the scattering of electrons is determined by the electrostatic potential of the atom, which depends on the charge distribution in the crystal. We have the relation[6] between the amplitude of the scattering of electrons and X-rays:

$$f_{el}[(\sin\theta)/\lambda)] = \frac{8\pi^2me^2}{h^2}\cdot\frac{Z - f_p[(\sin\theta)/\lambda]}{[(\sin\theta)/\lambda]^2}, \quad (7)$$

where $h$ is the Planck constant, $e$ and $m$ are the charge and mass of the electron, and $Z$ is the atomic charge. Using the values on the X-ray $f$ curves refined on the basis of experimental data (see below), it is possible to calculate $f_{el}$ more accurately by Eqn.(7), which permits an improvement of the accuracy of the structural information.

In order to make use of the information derived from the diffraction experiments in the study of electron density, it is essential to relate $\rho$ directly to the measured radiation intensity. This can be done within the framework of the kinematic theory of diffraction taking into account the corresponding dynamic corrections.[6,9] If the homogeneous monochromatic X-ray beam is incident on a crystal, then the total measured intensity of the scattered radiation can be formulated as follows:

$$T(\mathbf{q}) = JK(e^2/mc^2V)^2v\lambda^3LP(1+\alpha)\cdot|yDF(\mathbf{q})|^2 + \sum_m p_m I_m(\mathbf{q}) + B, \quad (8)$$

where $\mathbf{q}$ is a vector whose coordinates are the Miller indices, $h$, $k$, and $l$ [it is the scattering vector $|\mathbf{q}| = 4\pi(\sin\theta)/\lambda$], $K$ a multiplier which takes into account the drift of the primary beam over a long period, $A(\mu)$ the transmission function which depends on the absorption coefficient $\mu$, $\alpha$ a correction for the thermal diffuse scattering, $V$ the volume of the unit cell, $B$ the background intensity, $p_m$ are coefficients taking into account the energy exchange between the incident and reflected beams with the intensities $I_m$ under the conditions of repeated scattering, $J$ is the intensity of the incident radiation with a wavelength $\lambda$ per unit area, $e^2/mc^2$ the electron multiplier, $v$ the volume of the crystal involved in the reflection, $P$ the polarisation multiplier, $L$ the Lorentz factor, $y$ the correction for extinction, and $D$ the correction for anomalous scattering.[6]

The formula for the intensities of neutron diffraction can be formulated analogously.[9] In this case the multiplier $e^2/mc^2$ is omitted from Eqn.(2) and, in view of the lack of polarisation of the neutrons, $P = 1$.

Eqn.(8) can be conveniently rewritten in the form

$$T(\mathbf{q}) = I(\mathbf{q})/M + \sum_m p_m I_m(\mathbf{q}) + B, \quad (9)$$

where $1/M = \text{KLP}(1+\alpha)A(\mu)$ and $I(\mathbf{q}) = |yDF(\mathbf{q})/k|$. The fact that $1/k^2 = J(e^2/mc^2V)^2\lambda^3$ is independent of $\mathbf{q}$ was used here; the quantity $K$ is a scaling factor. Evidently, the intensity of the Bragg reflection can be represented by the expression

$$I = M\left(T - \sum_m p_m I_m - B\right). \quad (10)$$

The factors influencing the accuracy of the determination of the intensities of the diffraction reflections and the moduli of the structural amplitudes can be divided into two types. The factors unrelated to the type of radiation (X-rays and neutrons) or depending on a given type but in terms details which are insignificant should be assigned to the first type. For example, as a result of repeated scattering, due to the fact that the reflecting site can contain simultaneously several inverse lattice sites, the intensity of the measured reflection changes. Such a change can be avoided when the crystal is rotated around the direction of the scattering vector until all the inverse lattice sites, except that for which the measurement is made, have passed out of the Ewald sphere. Factors of the first type also include the geometry of the measurement taken into account by the Lorentz multiplier.[6]

Factors of the second type, associated with various mechanisms of the interaction with X-rays and neutrons with the crystal, have to be taken into account in different ways (absorption, extinction, thermal diffuse scattering). The principal difficulties in the accurate determination of the structure amplitude arise in absorption when the test crystal has an arbitrary geometrical shape, in extinction in the case where the shape and size of the coherent scattering blocks in the specimen are markedly anisotropic, and in thermal diffuse scattering for crystals with a low symmetry.

The allowance for absorption when the radiation passes through the crystal reduces to the calculation of the integral[9]

$$A(\mu) = \frac{1}{v}\int_{v} \exp[-\mu(r_1 + r_2)]\, dv, \qquad (11)$$

in which $r_1$ and $r_2$ are the distances traversed by the beam in the crystal before and after diffraction. Here the accuracy of the determination of the average effective length of the path of the beam in the crystal for each *hkl* reflection is the most significant. For a spherical specimen, the corrections for absorption have been tabulated; for a polyhedral crystal, they can be calculated by a method which has been described.[7] The absorption coefficients for X-rays are in the range ~$10^2$–$10^3$ $cm^{-1}$, while those for neutrons are significantly smaller ($\mu \cong 10^{-1}$ $cm^{-1}$ for $\lambda \leq 1$ Å). Lithium, boron, cadmium. and certain lanthanides ($\mu_{neutr} \cong 10$–$100$ $cm^{-1}$) as well as substances whose composition includes a large number of hydrogen atoms ($\mu_{neutr} \cong 2$–$5$ $cm^{-1}$) are exceptons.[9]

Allowance for the deviations from kinematic diffraction due to the presence of excited states in the crystal lattice in the radiation field, which entails non-elastic coherent scattering by acoustic phonons or thermal diffuse scattering (TDS) is extremely important.[8,10] Allowance for this effect is especially important in neutron diffraction, where the energy of the neutrons used in the diffraction experiment is close to that of the thermal vibrations of the lattice atoms. The contribution by TDS to individual reflections in molecular crystals can reach 30% of the intensity of the Bragg peak.

For certain relations between the velocities of the thermal neutrons and sound in the crystal, the effective cross-sections for the TDS of neutrons and X-rays can become comparable. For example, for lead and similar "soft" materials, the TDS for neutrons and X-rays become similar when $\lambda_{neutr} \leq 1.70$ Å while for "hard" materials (tungsten and others) this happens already for $\lambda_{neutr} \leq 0.77$ Å.

The correction for TDS can be represented in the form

$$1 + \alpha = \exp[2\Delta U[(\sin\theta)/\lambda]^2], \qquad (12)$$

where $\alpha$ is the ratio of the intensities of the thermal diffuse and Bragg scattering and $\Delta U$ is the effective temperature coefficient common to all the atoms of the structure. Evidently the neglect of the TDS effect leads to errors in the determination of the atomic thermal parameters manifested by their apparent decrease.

Several methods have been proposed for the calculation of corrections for TDS which are suitable in the case of crystals of any symmetry.[8,10] The effect can also be diminished by reducing the experimental temperature. For example, $\Delta U \cong 0.1$ Å$^2$ for ammonium oxalate $(NH_4)_2C_2O_4$ at room temperature, while at $T = 110$ K the quantity $\Delta U$ decreases to 0.04 Å$^2$. However, the use of low temperatures presupposes the thermal stability of the crystal and the absence of phase transitions in the latter. One should note that the contribution of TDS depends significantly on the conditions of the measurements: the divergence and the non-monochromatic nature of the primary beam, the aperture of the detector, the size of the crystal investigated, and the methods used to correct the background and the quantity q.[10]

As an example, Fig. 2 presents the dependence fo the TDS contribution on $(\sin\theta)/\lambda$ and the aperture of the counter for the scattering of X-rays by a ruby single crystal.[10] Such data make it possible to select the optimum strategy for precision intensity measurements.

After the above corrections have been introduced, it is possible to formulate a formal expression for the estimation of the variance of the measured intensity:

$$\sigma^2(I) = Q^2\sigma^2_{cr} + Q^2p^2I_0^2 + s^2(Q)\, I_0^2, \qquad (13)$$

where $\sigma^2_{st}$ takes into account the statistical components of the variance (the radiation quanta registered by the counter obey the Poisson distribution[11]), $Q$ is determined by comparing the intensities of periodically measured references reflections, $s^2(Q)$ is the random variance of $Q$, the multiplier $p$ takes into account the instrumental instability of the error associated with the application of the corrections and partly with the random errors that have not been taken into account. An estimate of the accuracy of the measurement is also provided by averaging the symmetrically-equivalent reflections measured over the total Ewald sphere; the extent of the scattering is an index of the accuracy of the experimental determination of the extent of diffraction intensities.[12]

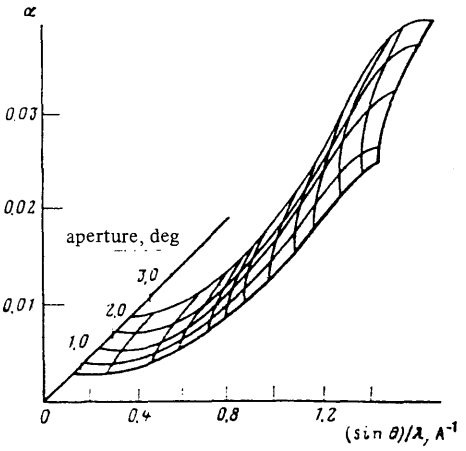



**Figure 2.** The influence of thermal diffuse scattering on the intensity of X-ray diffraction by a ruby single crystal.[10]

The primary treatment of diffraction data described above makes it possible to proceed to the elucidation of the structure of the crystal and then to its refinement by the method of least squares. Here it is necessary to take into account extinction and anomalous scattering. The correction for extinction allows for the change in the reflection intensity owing to the phase relations between the rays scattered by different points in the crystal. The correction is applied by introducing in Eqn. (8) the multiplier $y = y_1y_2$. The correction for the primary extinction $y_1$ takes this effect into account in each of the mosaic blocks and the correction for the secondary extinction $y_2$ takes it into account for the entire collection of these blocks. Corrections of the two types are inter-related—in particular $y_2 \approx f(y_1)$,[12] and only the quantity $y_2$ is therefore usually included among the parameters refined by the method of least squares.[13]

Anomalous scattering arises when the frequency of the incident radiation is comparable to the intrinsic frequencies of the vibrations of the scattering atom in the crystal. In this case the expression for the atomic amplitude is[7]

$$f=f_0+\Delta f'+i\Delta f'', \qquad (14)$$

where $f_0$ is the normal scattering component and $\Delta f'$ and $\Delta f''$ are corrections taking into account the anomalous scattering. The values of these corrections at the X-ray wavelengths normally employed in the structural analysis for light atoms are small, but for heavy atoms they can reach 5–10% of $f_0$. In neutron diffraction the correction for anomalous scattering is significant only for nuclei such as $^6$Li, $^{10}$B, $^{113}$Cd, and certain lanthanides. The methods used to apply this correction have been described in detail and the corresponding tables of the values of $\Delta f'$ and $\Delta f''$ have been published.[14,15]

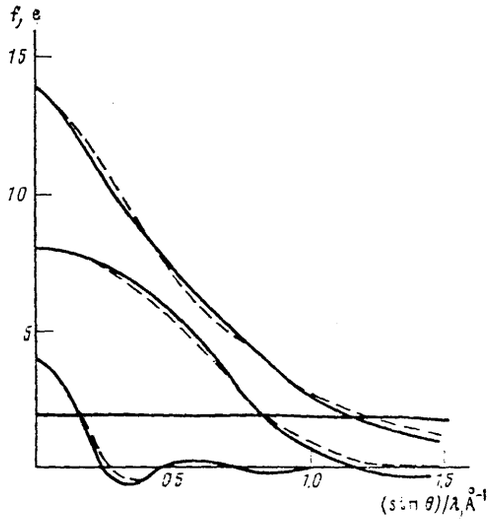



Figure 3. The atomic [$f = f_K + f_L + f_M$ (1)] and partial [$f_K$ (2), $f_L$ (3), and $f_M$ (4)] scattering amplitudes for the Si atom calculated using Slater orbitals (continuous lines) and Hartree–Fock orbitals (dashed lines).[16]

We shall now consider certain features of the procedure involved in the application of the method of least squares in connection with the problem of the determination of the electron distribution in crystals. The positional (coordinates) and thermal parameters of atoms, the scaling factor $k$ which converts the experimental data to values in terms of the absolute scale, and the correction for extinction are refined by this method. The deficiencies of the model of spherically symmetrical atoms have already been mentioned above. The error in the refinement procedure can be diminished, for example, by taking into account the fact that the electrons of the valence subshells deformed by chemical bonds scatter X-rays mainly in the "short-range" region of the inverse space. Fig.3 presents the atomic amplitude calculated using Slater type orbitals (STO) in terms of the orthogonal basis set and the basis set of the Hartree–Fock (HF) orbitals for the silicon atom[16] having the electronic configuration $1s^22s^22p^63s^23p^2$. It is also seen from Fig.3 that, when the basis set is altered, the partial amplitudes indicate an apparent "flow" of densities from one shell to another. This must be taken into account by comparing the experimental and quantum-chemical results of the determination of electron density distribution: the application of identical basis functions in both cases is an obligatory condition for the correct interpretation of the results.

The coordinates and thermal parameters of atoms are usually refined on the basis of "long range" reflections where the contribution due to spherically symmetrical (undeformed) inner electron subshells is mainly manifested.[17] Here it is assumed that the boundary between the "long-range" and "short-range" regions of the inverse space is located at $(\sin\theta)/\lambda \cong 0.7–0.8$ Å$^{-1}$. However, one should bear in mind that the non-spherical characteristics of the valence subshells (for example, the unshared electron pairs) make an appreciable contribution to the scattering up to $(\sin\theta)/\lambda \leqslant 1.0$ Å$^{-1}$.[5] Instead of refining the thermal and positional parameters of atoms, we can also determine them in an independent neutron diffraction experiment.

In accurate studies the modification of the electron density of atoms in the crystal is taken into account approximately by introducing into the radial part of the function describing the density of valence electrons the multiplier $\kappa$ which characterises its "contraction" or "expansion" compared to the free atom.[18] In this case the scattering amplitude for valence electrons is defined by the expression

$$f_{val}(\varkappa, q)=f'(q/\varkappa), \qquad (15)$$

where $f'$ is the amplitude of the scattering by the free atom.

The parameter $\kappa$ and the populations of the valence shells of atoms are included among the parameters refined by the method of least squares. An even greater flexibility can be achieved by employing a multipolar model. Within the framework of this model, the electron density of the bound atom in the crystal is represented by the expansion in terms of the angular harmonics $y_{\ell}(\theta, \phi)$ satisfying the local symmetry of the environment (see below). This model diminishes significantly the $R$ factor#[13] and other criteria for the statistical estimation of the reliability of the results.[19]

Allowance for a series of physical and chemical requirements, such as the electroneutrality of the crystal, the equality of the parameters referring to chemically equivalent parts of the molecules, and the imposition of limitations on the components of the thermal vibrations owing to the rigidity of the bond,[20] is also extremely useful and makes it possible to reduce the error of the results.

## III. METHODS FOR THE REPRESENTATION OF ELECTRON DENSITY

In the study of the characteristics of the electron distribution in a system made up of atoms linked by chemical interactions, it is convenient to make use of difference functions of the type

$$\delta\rho(r)=\rho_1(r)-\rho_2(r), \qquad (16)$$

where $\rho_1$ and $\rho_2$ are functions corresponding to two different

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#The unreliability factor $R$ is used to estimate the relative error in the refinement of the structure of the crystal and is calculated from the formula $R = \sum_q[F_{exp}(q) - F_{calc}(q)]/\Sigma F_{exp}(q)$, where $F_{exp}$ and $F_{calc}$ are the measured and calculated structural amplitudes respectively.

versions of the determination of the electron distribution. The experimental electron density $\rho_{exp}$ is normally employed as $\rho_1$.

The function of the deformation electron density

$$\delta\rho(\mathbf{r}) = \rho_{exp}(\mathbf{r}) - \sum_n \rho_n(\mathbf{r}), \qquad (17)$$

is most convenient for the analysis of the redistribution of electrons in the system caused by the involvement of atoms in chemical bonding. Here the sum represents the electron density for a set of spherically symmetrical atoms located at the same point as the atoms in the crystal (the electron density of the "promolecule").[21]

If only the inner electrons (electronic skeletons) of atoms are involved in the summation, then the function $\delta\rho$ describes the valence electron density of the crystal.

Eqn.(17) can be rewritten in terms of the series

$$\delta\rho(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{q}} \delta F(\mathbf{q}) \exp(-i\mathbf{qr}), \qquad (18)$$

where $\delta F(\mathbf{q}) = F_{exp}(\mathbf{q}) - F_{calc}(\mathbf{q})$ and $F_{calc}(\mathbf{q})$ is the Fourier transform of the electon density of the promolecule.

The theoretical calculation should be performed using modern quantum-chemical methods[3] taking into account the relativistic effect and multiconfiguration interaction; otherwise the low accuracy of the calculation can hinder the interpretation of $\delta\rho$. However, since this is not always feasible, one can employ wave functions calculated with the aid of the relativistic version of the Hartree–Fock method; the corresponding $f$ curves have been tabulated.[7]

The function $\delta\rho$ can be regarded as one describing the redistribution of electrons in the system due to chemical bonding. Naturally the diffraction data must be interpreted in terms of the same basis set as in the calculation for the promolecule taking into account the modification of the wave functions of the valence electrons.

The graphical representation of the cross-sections of the deformation electron density function for the test molecules makes it possible to determine whether the chemical bonds are straight or bent (strained) and directional or of the many-centre type, what their shape is in cross-section, where the unshared electron pair density maxima are located, how the deformation of the electron density of the atom depends on its environment, etc.

As an example, Fig.4 presents the results of a precision study of a ruby crystal having the composition $Al_2O_3$ + Cr(0.46 wt.%).[22] Fig.4*a* illustrates the map of the deformation electron density of a fragment of the structure of ruby containing characteristic Al–O bonds 1.970 and 1.856 Å long. The map contains excess deformation (covalent) peaks whose height is approximately 0.27 eÅ$^{-3}$ which have undergone a shift towards the more electronegative O atom and which have been displaced from the line of the bond. This map shows that the Al–O bonds in ruby and also in corundum $Al_2O_3$ are partly covalent and strained and the shift of the deformation peak from the line of the bond is a consequence of the electrostatic interaction of the electrons in the region of the bond with the nearest "foreign" positively charged ion. It can be seen that distinctly directional individual chemical bonds characteristic of ionic crystals are absent from the structure, while the electron density is highly localised. These features of the electronic structure are reflected in the properties of ruby such as, for example, its mechanical strength.

In the study of ruby[22] an attempt was made to determine by X-ray diffraction the positions of the $Cr^{3+}$ ions. Refinement by the least squares method ($R$ = 0.0068) showed that the chromium ion, substituting the $Al^{3+}$ ion in the structure isomorphously, is not located exactly at the position of the latter but is displaced along the hexagonal $z$ axis by 0.13 Å towards an octahedral vacancy. A difference electron density map has been constructed (Fig.4*b*) on which the admixture of $Cr^{3+}$ ions appears in the form of an excess peak 0.3 eÅ$^{-3}$ high in the vicinity of the $Al^{3+}$ ions. The possibility of determining such a small amount of the admixture is characteristic of the actual attainable accuracy of modern diffraction methods.

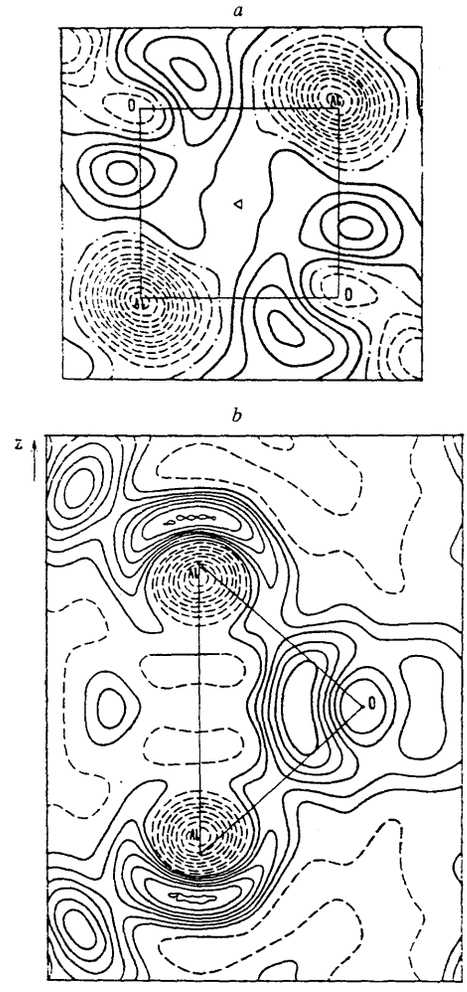



**Figure 4.** Fragments of deformation electron density in the ruby crystal.[22] (Here and henceforth the continuous lines on the map connect points with excess electron density, the dashed lines connect points with deficient electron density, and the dash-dot lines connect points with zero electron density): *a*) sections through the Al and O atoms and the centre of symmetry; the spacing between lines 0.07 eÅ$^{-3}$; *b*) the (0110) [sic] plane; the Cr atom was not removed in the synthesis and can be seen as a peak above and below Al; the spacing between lines is 0.05 eÅ$^{-3}$.

The deformation electron density function can be constructed in accordance with two schemes.[23,24] In the first of these all the parameters for the calculation of $F_{calc}$ were

obtained by refining the X-ray diffraction data corresponding to high experimental values of $(\sin\theta)/\lambda$ (the $X-X$ method). In the second $F_{calc}$ is determined with the aid of parameters obtained from a neutron diffraction experiment (the $X-N$ method). As stated above, the advantage of the latter consists in the absence of a dependence of the results of the measurements of the model of the electronic structure of the crystal and in the reliability of the determination of the positional and thermal parameters of light atoms (in the first place hydrogen) in the presence of heavy atoms.

The application of the $X-N$ approach requires allowance for the specific features of both diffraction methods and also for the possible difference between the temperatures of the two experiments.[12,23] A check on the temperature can be carried out by calculating the unit cell parameters of the crystal, which should be identical at identical temperatures. It is more difficult to take into account other effects. For example, TDS is manifested in different ways in experiments of the two types: in neutron scattering the contribution of TDS is greater. This reduces the thermal parameters of the atoms obtained in neutron diffraction experiments by approximately 10% relative to the X-ray experiments. Next, discrepancies arise in the results due to the differences in the allowance for the background in the calculation of the contribution of elastic scattering to the intensity. Furthermore, the different sizes of the crystals and the difficulty of an adequate description of the X-ray and neutron scattering processes also lead to errors which cannot be always fully corrected. Practical procedures used in such corrections can be found in a number of communications.[1,12,23]

In order to obtain reliable results in the analysis of the function $\delta\rho$, the error in the deformation density $\sigma(\delta\rho)$ must be less than the significant details in the function $\delta\rho$. On the basis of the standard deviations of the parameters obtained as a result of the least squares refinement and $\sigma^2(F_{exp})$, the variance of the deformation electron density can be represented in the form[23,25]

$$\sigma^2(\delta\rho) = \frac{2}{V^2}\sum_{|q|>0}[\sigma^2(\delta F)\cdot\cos^2\alpha + \delta F^2\cdot\sin\alpha\cdot\sigma^2(\alpha) + \\ + \sin 2\alpha\cdot\delta F\cdot\sigma(\delta F)\cdot\sigma(\alpha)\cdot\gamma(\delta F,\alpha)], \qquad (19)$$

where $\alpha = qr - \beta$, $\beta$ is the $\delta F$ phase, and $\gamma$ the correlation coefficient.

As a result of a careful study, it is possible to express $\sigma^2(\delta\rho)$ in terms of $\sigma^2(F)$, $\sigma^2(F_{calc})$, and $\sigma^2(k)$ and to show that (1) the error due to $\sigma^2(F)$ and $\sigma^2(F_{calc})$ is approximately constant throughout the cell and does not exceed 0.04 eÅ$^{-3}$ for centrosymmetrical structures with light ($Z \leq 16$) atoms and 0.06 eÅ$^{-3}$ for non-centrosymmetrical structures and (2) the error due to $\sigma^2(k)$ and the errors in the structural parameters is significant only in the vicinity of the centres of atoms and for heavy ($Z \geq 50$) atoms reaches in this instance 6–8 eÅ$^{-3}$, while for light atoms it is 0.1–0.8 eÅ$^{-3}$. In the $X-N$ scheme the error associated with the inaccurate selection of the amplitude of the coherent neutron scattering can also have an effect; in the vicinity of the centres of atoms it is comparable in magnitude to the errors due to other factors and must be taken into account.[26]

The average error of the determination of the deformation electron density, constructed on the basis of precision diffraction data, is usually less than 0.05 eÅ$^{-3}$ in the region of the chemical bond.[1] This makes it possible to investigate at the present time the details of the electron distribution in crystals containing heavy atoms (up to $Z = 78$). Such accuracy and the potential set of objects, including complex molecules with heavy atoms, are so far inaccessible to theoretical calculations.

Another field where diffraction data are used involves the determination of the numerical characteristics of the electron distribution. Several methods have been proposed for the solution of this problem and these have been described in detail, for example, by Tsirel'son and Ozerov.[23] The simplest method of parametrising the function $\rho(\mathbf{r})$ consists in determining the electronic charge concentrated in a certain volume by the direct integration of the function $\rho$ over this volume. In particular, it is possible to estimate in this way the effective atomic charges. Usually the volume over which the integration is carried out is represented by a sphere bounded by the minimum of the function $\rho$; this approximation is justified only for a simple ionic compound.[24] In the case of atoms involved in covalent bonds, it is useful to employ more complex methods for charge separation. In the integration, account must also be taken of the fact that the function $\rho$ is constructed on the basis of data obtained in a diffraction experiment in which only a limited number of terms of the Fourier series are measured; the appropriate correction must therefore be applied to the final results.[27]

Table 1. The atomic charges in certain silicates.[28]

| Atom | $Mg_2Si_2O_6$ | $Co_2Si_2O_6$ | $Fe_2Si_2O_6$ | $Mg_2SiO_4$ | $Co_2SiO_4$ | $Fe_2SiO_4$ |
|---|---|---|---|---|---|---|
| Metal, $M(1)$ | +1.84 (4) | +1.29 (11) | +1.14 (12) | +1.76 (3) | +1.60 (11) | +0985 (8) |
| Metal, $M(2)$ | +1.79 (4) | +0.81 (12) | +1.10 (13) | +1.74 (3) | +1.54 (7) | +1.45 (11) |
| $Si^A$ | +2.20 (4) | +1.79 (9) | +2.21 (11) | +2.11 (3) | +2.21 (10) | +2.43 (6) |
| $Si^B$ | +2.36 (4) | +2.76 (9) | +2.16 (11) | — | — | — |
| $O(1)^A$ | −1.51 | −1.10 | −1.04 | −1.52 | −1.24 | −1.13 |
| $O(1)^B$ | −1.37 | −1.14 | −1.19 | — | — | — |
| $O(2)^A$ | −1.36 | −1.12 | −1.09 | −1.29 | −1.24 | −1.21 |
| $O(2)^B$ | −1.43 | −1.16 | −1.20 | — | — | — |
| $O(3)^A$ | −1.31 | −0.84 | −0.92 | −1.40 | −1.39 | −1.24 |
| $O(3)^B$ | −1.22 | −1.10 | −1.18 | — | — | — |
| ⟨Metal⟩ | +1.82 | +0.95 | +1.12 | +1.75 | +1.57 | +1.15 |
| ⟨Si⟩ | +2.28 | +2.28 | +2.19 | — | — | — |
| ⟨O*⟩ | −1.42 | −1.43 | −1.13 | — | — | — |
| ⟨O**⟩ | −1.27 | −1.05 | −0.97 | — | — | — |
| ⟨O⟩ | −1.37 | −1.08 | −1.10 | −1.40 | −1.29 | −1.19 |

Notation: The angular brackets indicate that average quantities are quoted; $M(1)$ and $M(2)$ are two types of octahedral and $A$ and $B$ are two types of tetrahedral positions in the structure.

*Non-bridging oxygen atoms.

**Bridging oxygen atoms.

The effective charges on the atoms in certain oxides and silicates obtained in this way[27,28] are listed in Table 1. In conformity with modern ideas concerning the semicovalent character of the chemical bond, the charges on the oxygen ion in the oxide compounds are in the range from −0.8 to −1.5 e and those on the silicon atoms are from +1.8 to +2.8 e.

Another way of estimating the atomic charges from diffraction data consists in the application of the method of least squares.[29] For this purpose, the atomic electron shells are assumed to consist of a constant inner part to which a fixed number of electrons are bound and of the valence part whose electron population is to be refined. Simultaneously with the refinement of the number of valence electrons, it is possible to take into account, using the parameter $\kappa$ and Eqn.(15), the radial modification of the valence electron shell associated with the charge redistribution in the system.[18]

A correlation has been observed between the charge on the atom and the parameter $\kappa$,[18] which agrees well with the familiar Slater rules for the selection of the exponential multipliers in the radial parts of the orbitals. Fig.5 shows that these simple rules make it possible to determine quite satisfactorily the charge on the N atom in various organic compounds; this can also be said of the C and O atoms.

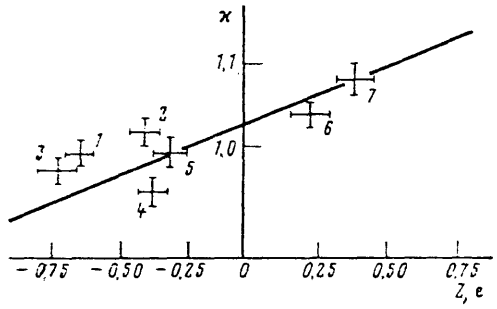



Figure 5. Dependence of $\kappa$ on the atomic charge according to Coppens et al.:[18] 1) and 2) glycylclycine; 3) formamide; 4) cyanuric acid; 5) tetrasulphotetranitride; 6) sulphamic acid; 7) *p*-nitropyridine *N*-oxide; the result of the calculation by the Slater method is indicated by the straight line.

We shall consider the multipolar procedure for the refinement of structural parameters by the least squares method. In this approach the electron density of the crystal is represented in the form

$$\rho(\mathbf{r}) = \sum_j \left\{ \rho_j(\mathbf{r}) + \sum_i c_{ij} R_{ij}(\mathbf{r}) \Phi_{ij}(\theta, \varphi) \right\} \qquad (20)$$

where $\rho_j$ is the electron density on the $j$th atom, according to Hirshfeld and Harel,[30,31] or on the skeleton of this atom, according to Stewart,[32] and the $c_{ij}$ are the coefficients of the expansion (the electron "populations") of the multipoles.

Eqn.(20) represents the expansion of the deformation of the valence electron density in terms of functions whose angular component $\Phi_{ij}$ describes the multipolar (dipolar, quadrupolar, octapolar, etc.) deformation of the atom in the crystal, determined by the symmetry of the environment and the effects of the chemical interaction. The radial functions usually have the form

$$R_{ij}(r) \sim r_{ij}^n \exp(-2\alpha_{ij} r_{ij}),$$

where $r_{ij}$ is the current coordinate reckoned from the nucleus of the $j$th atom.

Thus the electron density of the crystal is represented by the sum of the multipolar terms ("pseudoatoms"[32]) and the coefficients and the experimental multipliers of the multipoles $\alpha_{ij}$ are included among the parameters refined by the least squares method. This model is very flexible, and its flexibility can be increased still further by combining the multipolar expansion method with the use of the parameter $\kappa$.[19] The electron populations of the monopolar terms are usually interpreted as the electronic charges on the atom. A direct interpretation of the remaining multipolar parameters of the electron density distribution in terms of the LCAO-MO approximation is difficult.

The multipoles linked by the *d* orbitals of transition metal atoms are an exception.[33] Information of this kind is of considerable interest. Thus it follows from the refinement of the above populations of the cobalt atom in (*meso*-tetraphenylporphyrinato)cobalt(II) ($C_{44}H_{28}N_4Co$),[34] carried within the framework of the crystal field theory, that the cobalt atom in this compound exists in a low-spin state, in conformity with the results of magnetic measurements (Table 2).

Table 2. The electron populations of the *d* levels of cobalt in $C_{44}H_{28}N_4Co$.[34]

| Atomic orbital | Electron populations | | | |
|---|---|---|---|---|
| | I | II | III | III |
| $b_1 (d_{x^2-y^2})$ | 1.4 | 0.0 | 1.0 (2) | 0.25 |
| $a_1 (d_{z^2})$ | 1.4 | 1.0 | 1.0 (2) | 1.06 |
| $b_2 (d_{xy})$ | 1.4 | 2.0 | 1.3 (2) | 1.76 |
| $c (d_{xz}, d_{yz})$ | 2.8 | 4.0 | 3.7 (3) | 3.91 |

Notation: I) the expected high-spin state; II) the ideal low-spin state; III) results of refinement on the basis of diffraction data; IV) theoretical calculation by the configuration interaction method.

The observed deviation from the expected values indicates the limited applicability of the one-determinant approximation for the description of the observed picture. Comparison with theoretical calculations (Table 2) show that, when the additional excitations of the electronic configurations are taken into account, the theoretical populations of the 3*d* orbitals vary in parallel with experimental data. Another important result of Stevens' study[34] is the demonstration of the limited character of the crystal field theory, which is frequently used to interpret the state of the metal ion in organometallic [sic] compounds.

In particular, the unduly high populations of the $d_{x^2-y^2}$ orbital which follow from the diffraction data are a consequence of the failure to take into account the metal–ligand $\sigma$-bond by this theory, while the neglect of the $\pi$ interaction leads to reduced populations of the $d_{xy}$ and $d_{yz}$ orbitals.

The large number of parameters of the multipolar model entails their strong mutual correlation in the equations of the least squares method. In order to increase the reliability of the results of the multipolar method of calculation, it is useful to introduce certain additional conditions relating the parameters being refined to one another. For example, it is possible to carry out the refinement in such a way that agreement is ensured between the electric field gradient at one of the atomic nuclei and the value derived from NQR experiments. A refinement of this kind, carried out for aluminium phosphate ($AlPO_4$)[35] showed that the above procedure makes it possible to attain a deeper minimum in the functional (3) for the charges on the Al, P, and O atoms; values of +1.4, +1.0, and −0.60 e respectively were obtained. These charges indicate a significant covalence of the P–O bond, which has also been confirmed by the cross-sections of the deformation electron density function constructed by Schwarzenbach and Ngo Thong.[35]

The multipolar analysis of the distribution of electron density in diamond and graphite has shown that the exponential multiplier in the radial function $\alpha_{exp}$, found by least

squares refinement, is 1.56 for diamond[36] and 1.58 for graphite,[37] whereas for the free carbon atom $\alpha = 1.59$.[38] Comparison of these data with the molecular optimised value $\alpha_m = 1.72$, obtained for the carbon atom by averaging the results of quantum-chemical calculations in terms of the minimal basis set for a series of simple organic molecules,[38] has shown that the calculated $\alpha$ corresponds to a more "contracted" atom. An analogous situation has been observed for silicon ($\alpha_{exp} = 1.6$; $\alpha_m = 1.75$).[38] Comparisons of this kind are useful for semiempirical quantum-chemical calculations where there is a possibility of choosing the optimum values of the exponential multipliers, defining the basis functions, depending on the level of the approximations adopted. Thus one may conclude that in quantum-chemical calculations where the overlap of orbitals of neighbouring atoms is neglected it is possible to compensate for the failure to allow for the shift of part of the electron density to the interatomic space by reducing the values of $\alpha$ in terms of the minimal basis set.

Maps of the deformation electron density can be constructed on the basis of the results of the multipolar refinement. Such "synthesised" maps filter out the "noise" associated with the errors in the diffraction data and are to a large extent free from the defects due to the cut-off of the Fourier series.[19] As an example, we shall consider the compound $C_{44}H_{28}N_4Co$ mentioned above.[34] Fig. 6*a* presents the cross-section of the multipolar function $\delta\rho$ in the plane of the pyrrole ring averaged with respect to the chemically equivalent parts of the molecule. The distribution of errors for the non-averaged case is illustrated in Fig. 6*b*; the error in the determination of the distribution of the centres of atoms reaches 0.7 eÅ$^{-3}$ according to the estimates made above. The "multipolar filtration" and averaging reduce this error by a factor of 3–4. Ultimately the characteristics $\delta\rho$ become even more pronounced: $\delta\rho > 3\sigma(\delta\rho)$. The peak on the C(2)–C(3) bond on the map, which significantly exceeds the peaks on other covalent bonds in the porphyrin molecule, is striking. This finding has been analysed[34] and accounted for in terms of the localisation of the $\pi$ electrons at this bond.

Another quantitative approach to the analysis of the electron distribution in crystals is based on the representation of $\rho(\mathbf{r})$ with the aid of the linear combination of atomic orbitals (LCAO) in the following form:

$$\rho(\mathbf{r}) = 2\sum_{ij} P_{ij}\varphi_i(\mathbf{r})\,\varphi_j^*(\mathbf{r}) \qquad (21)$$

where $\phi_i$ are the analytical atomic orbitals (for example, the orthogonalised Slater orbitals) and $P_{ij}$ are the elements of the charge–bond order matrix characterising the electronic structure of the system investigated. Having calculated the Fourier transform of formula (21), it is possible to find the matrix elements $P_{ij}$ assuming them to be adjustable parameters and minimising the functional (3). However, the attempt to apply such an approach in conjunction with the least squares matrix encountered computational difficulties associated with the correlation between the parameters to be refined.[39–44] This led to the use of the palliative methods mentioned above,[29] in which either certain matrix elements $P_{ij}$ were not refined, being selected *a priori*, or the electron populations of the valence shells of each atom were refined as one parameter. Nevertheless, the idea of the above approach is extremely primising because it leads to the possibility of a direct comparison of the experimental results with data obtained from quantum-chemical calculations in terms of the LCAO approximation involving the same matrix *P*.

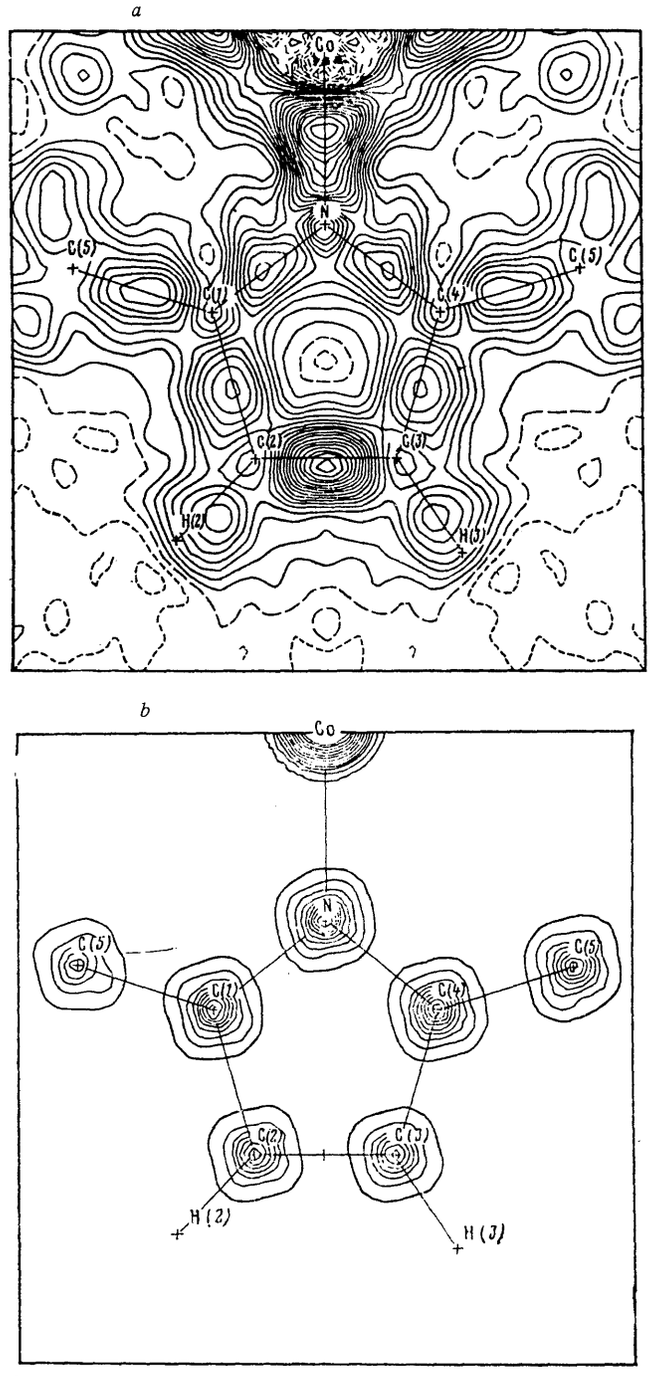



**Figure 6.** Deformation electron density for the $C_{44}H_{28}N_4Co$ crystal according to Stevens:[34] *a*) section in the plane of the pyrrole ring (spacing between lines 0.05 eÅ$^{-3}$); *b*) distribution of errors on the deformation electron density map (spacing between lines 0.02 eÅ$^{-3}$).

Analysis[45–47] has shown that, when the matrix elements $P_{ij}$ are sought, account must be taken of the quantum character of the electron distribution. In particular, it is essential that the quantities found should describe the distribution of electron density consistent with the Pauli

principle. Neglect of this fact can lead to negative electron densities in the vicinity of the nucleus or to populations of molecular orbitals exceeding 2e.[48] Allowance for it[47] led to equations for $P_{ij}$ having the same form as the equations for the same matrix in quantum chemistry (the Hartree–Fock–Roothaan equations). Thus the rigorous analysis made it possible to reduce to a single formal basis the experimental and theoretical approaches to the study of the distribution of electron density.

Table 3. The effective atomic charges in $HCOOLi.D_2O$.[49]

| Atom | Atomic charges, e | | |
|---|---|---|---|
| | experiment | *ab initio* calculation | EHM calculation |
| | Lithium ion | | |
| Li | 0.82 | 0.70 | 0.55 |
| | Formate ion | | |
| C | 0.04 | −0.01 | −0.01 |
| O (1) | −0.53 | −0.34 | −0.30 |
| O (2) | −0.46 | −0.34 | −0.26 |
| H | 0.13 | −0.02 | −0.02 |
| | Water molecule | | |
| D (1) | 0.11 | 0.06 | 0.08 |
| D (2) | 0.07 | 0.06 | 0.07 |
| O (3) | −0.18 | −0.12 | −0.10 |

Table 4. The intermolecular interaction energy $U_M$ and the heat of sublimation $\Delta H_S$ for the $HCOOLi.D_2O$ crystal.[50]

| Method of calculation | $U_C$, kcal mol$^{-1}$ | $U_M$, kcal mol$^{-1}$ | $\Delta H_S$, kcal mol$^{-1}$ |
|---|---|---|---|
| Diffraction data | 34.78 | 50.02 | 49.05±0.05 |
| Extended Hückel method | 8.36 | 24.10 | — |
| *Ab initio* calculation | 8.48 | 23.72 | — |

Remarks: $U_C$ is the Coulombic interaction energy; $\Delta H_S$ was measured on a Calvet microcalorimeter.

Calculations for the lithium formate deuterate ($HCOOLi.D_2O$) crystal[49] have shown (Table 3) that, although the experimental results agree with quantum-chemical data, there are also differences reflecting the effect of the crystal environment (both types of calculations have been carried out in terms of the same basis set). This has been manifested distinctly in the calculation of the intermolecular interaction energy in the $HCOOLi.D_2O$ crystal.[50] Calculation of this quantity by the method of atom–atom potentials taking into account the Coulombic interaction in terms of the "experimental" and quantum-chemical (for individual molecules) charges in the atoms revealed a satisfactory agreement with the results of thermodynamic measurements only when the "experimental" charges were used (Table 4). On this basis, one may conclude that the $P_{ij}$ matrix obtained from diffraction data describes satisfactorily the distribution of electron density in the crystal investigated. Theoretical calculations taking into account the crystal environment are not so effective.

## IV. THE ELECTROSTATIC FIELD IN THE CRYSTAL

The methods involving the "point" and parameteric representations of the electron density function using diffraction data were examined above. A concept according to which diffraction data are used to determine the electrostatic potential in crystal has developed recently.

The analytical expression relating the charge density functions for the electrons and nuclei of a system to the electrostatic potential of the point **r** is defined by the Poisson equation and assumes the following form:

$$\varphi(\mathbf{r}) = \sum_i (Z_i/|\mathbf{R}_i - \mathbf{r}|) - \int_{-\infty}^{\infty} \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}\, d\mathbf{r}, \qquad (22)$$

where $Z_i$ is the charge on the atomic nucleus located at the point $\mathbf{R}_i$. The first term in Eqn.(22) describes the contribution to $\phi(\mathbf{r})$ by the nuclei in the system and the second describes the contribution by the electron distribution. The function $\phi(\mathbf{r})$ characterises the electrostatic interactions between the unperturbed system and the positive unit charge at the point **r**. Eivdently the potential $\phi(\mathbf{r})$ can be useful in the description of the chemical interaction when the molecules are separated by large distances, whereupon one can neglect the polarisation, charge transfer, and exchange effects.

Numerous chemical applications of this approach have been dealt with in detail in a communication.[51] However, the deformation electrostatic potential (DESP), introduced by Varnek et al.[52] and Spackmann and Stewart,[53] contains no less information and is defined by the expression

$$\delta\varphi(\mathbf{r}) = \int_{-\infty}^{\infty} \frac{\delta\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}' = -\frac{4\pi}{V} \sum_{\mathbf{q}} \frac{\delta F(q)}{|q^2|} \exp(-i\mathbf{q}\mathbf{r}). \qquad (23)$$

From the physical point of view, DESP characterises the electrostatic field, which, when superimposed on the electrostatic field of the promolecule, ensures a stable equilibrium configuration of the system.

Fig.7, obtained for ruby, shows that DESP reflects its physical properties.[22] In particular, the delocalisation of electron density discussed above leads to an unusual distribution of the electrostatic potential in the ruby crystal. The regions near the centres of the aluminium atoms, where the positive potential of the incompletely shielded nuclei predominates in the crystal, giving rise to quasi-continuous bands between which are included regions of negative potential extended along the Al...Al bond. Such distribution of DESP reproduces the characteristics of the electrostatic interaction of the ions in the ruby crystal and can be associated with its mechanical strength.

The electrostatic potential determines the electric field and its gradient at any point within the crystal. The knowledge of the latter is particularly important at the sites where the nuclei of the system are located, because this makes it possible, in principle, to calculate the nuclear quadrupole moment from the diffraction data without resorting to its measurement by the NQR method of with the aid of the Mössbauer effect.[54] Comparison of such results, obtained with the aid of various methods, can serve as a significant criterion of the quality of the determination of the electron distribution. The joint application of both methods in the multipolar refinement was discussed above for $AlPO_4$.[35]

The most promising applications of the experimental electrostatic potential were apparently associated with the development of the concept of a density functional based on the Hohenberg–Kohn theorem[55] and its generalisation.[56,57] According to this theorem, the energy and other characteristics of the many electron system are fully determined by

the function $\rho$. The exact form of this functional has not been established, but there exist many approximate relations which enable one to express the energy of the system as a functional of $\rho(\mathbf{r})$[58] or $\phi(\mathbf{r})$.[59] The first attempt to include diffraction data within the framework of such an approach[52,60] indicates that this procedure is promising for the study of the properties of crystals.

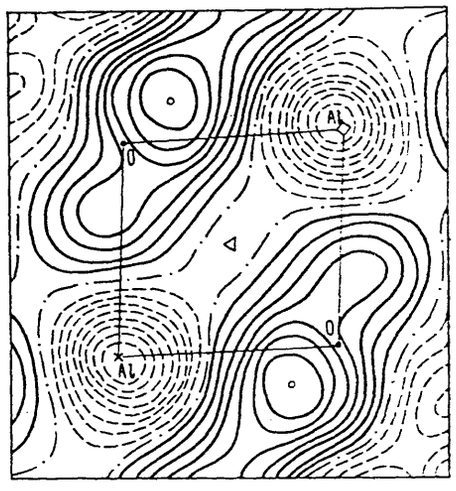



Figure 7. Experimental electrostatic deformation potential in ruby.[22]

## V. THE ATOMIC (ONE-PARTICLE) POTENTIALS

The deration of the elementary step of the interaction of radiation with matter is approximately $10^{-18}$ s and the characteristic time of thermal vibrations of lattice atoms is $10^{-12}$–$10^{-13}$ s. However, in real measurements the diffraction experiment yields a time-average picture of the crystal structure. As mentioned above, thermal movement is taken into account by introducing individual atomic temperature multipliers $W(\mathbf{q})$, which are the Fourier transforms of the distribution function $t(\mathbf{R})$ for the positions of the nuclei (neutrons) or the centres of gravity of the electron shells of the atom (X-rays). In the high-temperature limit (classical approximation), the above function can be written in the following form having replaced the time average by the average with res0ect to the ensemble:

$$t(\mathbf{R}) = \frac{\exp(-V(\mathbf{R})/kT)}{\int_{-\infty}^{\infty} \exp(-V(\mathbf{R})/kT)\,d\mathbf{R}}, \qquad (24)$$

where $V(\mathbf{R})$ is the potential energy of the atom vibrating in the effective force field of its neighbours. Such a one-particle model[61] constitutes a development of Einstein's model of independent oscillators.[62] If $V(\mathbf{R})$ is expanded in a power series in terms of displacements reckoned from the equilibrium position and the quasi-harmonic approximation is used,[61] then the expansion coefficients characterise the effective potential of the given atom. They can be included among the parameters capable of being refined by the least squares method and hence one can obtain important information about the dynamics of the crystal lattice. We may note that the above expansion is not restircted to the harmonic terms of the series and can be extended to higher-order terms associated with the asymmetry of the potential well.

There exists a fundamental relation between the function $\rho(\mathbf{r})$ and the effective atomic potentials, established by the Gel'man–Feynman theorem.[63,64] According to the latter, the force acting on each nucleus in the system is determined by the distribution of electron density and other nuclei. For the equilibrium configuration, this force becomes zero, which can serve as a criterion of the accuracy of the experimental distribution of electron density.

Diffraction analysis of the detailed characteristics of the lattice dynamics has become possible only very recently. Its first applications were associated with the study of the ionic conduction in solids.[65–68] For example, the form of the effective potential in lithium nitride ($Li_3N$) has been established[67,68] from X-ray diffraction data obtained over a range of temperatures. The above compound crystallises in the *P6/mmm* group, the N atom being surrounded by eight Li atoms in the form of a hexagonal bipyramid. Having applied the 6th-order Gram–Charlier expansion§, Schulz and Zucker[66,67] showed that the height of the potential barrier between the lithium atoms located in a plane perpendicular to the c axis is $0.29 \pm 0.04$ eV. Thus, the appearance of ionic conduction requires that the activation energy for the ion should be in the range 0.25–0.33 eV, which agrees with the results of the experimental measurement of this quantity (approximately 0.29 eV).[68]

Another application of the approach considered has been described in a study[69] where the concept of the effective atomic potential was applied in a correct interpretation of the deformation electron density maps for the $KCuF_3$ crystal subjected to Jahn–Teller distortion. In particular, it has been shown that the Coulombic attractive interaction between the $Cu^{2+}$ and $F^-$ ions exerts a greater influence on the anharmonicity of the vibrations of the $Cu^{2+}$ ion than the repulsion between the atomic skeletons.

The concept of effective atomic potentials has proved to be extremely useful also in other fields of study of the properties of crystals. Thus the parameters of the potentials can be related to the force constants of the chemical bonds and their characteristic frequencies, which makes it possible to relate the diffraction and spectroscopic analytical methods. Furthermore, knowledge of potential function character in the vicinity of atomic centres combined with knowledge of the details of the electron distribution in crystals is essential for understanding the mechanism of chemical reactions in the solid phase and also for controlling these reactions.[70] The establishment of relations of this kind is a task for the future and the immediate development of this field holds out very much promise.

## VI. CHARACTERISTICS OF THE ELECTRONIC STRUCTURE OF CRYSTALS OF DIFFERENT TYPES

The possibilities of modern diffraction methods for the study of the electronic structure and properties of crystals were demonstrated above. It is important, in principle, that $\rho$ is the observed experimental quantity which can be visualised by a graphical representation. This function contains important information about the properties of matter and with its aid it is possible to formulate a number of tasks

§ Other versions of the expansion of the potential are also possible—see, for example, Zucker and Schulz.[65]

involving the properties of the ground states of molecules and crystals.[71] The first attempts to apply this approach to the determination of certain magnetic and optical properties of crystals have already demonstrated its effectiveness.[71]

Analysis of the electron density function makes it possible to reinterpret the classical concepts of crystal chemistry. This applies particularly to the problem of the "dimensions" of atoms in the crystal and the possibility of an experimental estimation of their "radii" and "charges". In crystals with maximum covalent and metallic character, the atomic radius is determined simply as half the shortest interatomic distance and the effective charge within the limits of a sphere defined by such a radius can be logically assumed equal to zero.

However, analysis of the electron density distribution even in such simple crystals indicates a deviation of the form of the atoms in the crystal from the spherical shape. For covalent crystals of the type of diamond, the existence of electron density "bridges" between the atoms, surrounding one another in a tetrahedral arrangement has long been established. This picture corresponds to the model involving the $sp^3$ hybridisation of the valence orbitals of carbon and its analogues proposed by Pauling as early as 1929. It has recently been found that a situation similar to that already described is observed in metals and that a fraction of the valence electrons are localised along the length of the M–M bond.[72] The problem of the determination of the size of atoms in complex chemical compounds gives rise to even greater difficulties even when data concerning the distribution of electron density are available.

In order to obtain the dimensions of the ions from the function $\rho$, the criterion of the electron density minimum, characterised by the optimum separation radius $R_{sep}$, has been put forward.[27] It was found that the experimental values of $R_{sep}$, determined along the line of the bond, are intermediate between the classical and ionic and covalent (atomic) radii even in the most ionic compounds such as halides and oxides.[24] There are two main reasons which can account for this phenomenon:[73] (1) the anisotropic expansion of the electron shell of the cation and the contraction of the electron shell of the anion in the crystal and (2) the incompletely ionic character of the chemical bond. The first factor, which was initially predicted theoretically, was subsequently repeatedly confirmed also experimentally and with the aid of accurate calculations for alkali metal halides, where the bond can be regarded as virtually purely ionic. For these compounds, the experimental radii of the cations are greater by approximately 0.2 Å and those of the anions are smaller by the same amount from the classical ionic radii. This systematic difference is confirmed by the data presented in Table 5. It can be attributed wholly to the effects of the "contraction–expansion" of the ion in the crystal field and of the transfer of charge ensuring the fulfilment of the Pauli principle.

For multicharged ions in halides, oxides, and chalcogenides, these effects cannot be regarded as the only cause of the difference between the experimental maximum separation radii and the classical ionic radii. This is also indicated by the experimental estimates of the effective atomic charges obtained from the distribution of electron density, which were described above. In conformity with data obtained by other methods, these results indicate a semicovalent character of the chemical bond in the oxide and silicates of bivalent and tervalent elements. Experiment has shown that the Si–O bonds in silicates are more than half-covalent. On the other hand, chalcogenides are more correctly regarded as covalent compounds with a proportion of ionic character. This means that the concept of ionic radii cannot be strictly speaking applied at all to compounds of this group. Indeed, the results of numerous studies have shown that the optimum separation radii for the oxides and silicates are intermediate between the ionic and atomic radii and in many instances (Si, Al, Co, and Ni) they are closer to atomic radii than to ionic radii.

**Table 5.** Comparison of the radii of optimum separation of the electron densities of ions with the classical ionic radii ($R_i$) and atomic radii ($R_{at}$) in certain halides.

| Element | $R_i$, Å | $R_{sep}$, Å | $R_{at}$, Å | Refs. |
|---|---|---|---|---|
| $Na^+$ | 1.02 | 1.21±0.05 | 1.80 | [74] |
| $Cl^-$ | 1.81 | 1.61±0.05 | 1.00 | |
| $K^+$ | 1.38 | 1.45±0.07 | 2.20 | [74] |
| $Cl^-$ | 1.81 | 1.70±0.07 | 1.00 | |
| $Ag^+$ | 1.15 | 1.03±0.05 | 1.60 | [74] |
| $Cl^-$ | 1.81 | 1.74±0.05 | 1.00 | |
| $Ag^+$ | 1.15 | 1.13 | 1.60 | [75] |
| $Br^-$ | 1.46 | 1.76 | 1.15 | |
| $Mg^{2+}$ | 0.72 | 0.90 | 1.50 | [76] |
| $F^-$ | 1.33 | 1.25 | 0.50 | |

The idea of the continuous variation of the effective atomic size as the character of the chemical bond is varied between two limiting values—the ionic radius for the limiting ionic bond and the covalent radius for the covalent bond—is permissible. A linear variation of the radius with the amount of the ionic character of the chemical bond has been postulated. It was later shown that the variation of the dimensions of the electron shells (the so-called orbital radii) with the charge is not strictly linear.[73] Having adopted this model, one must not forget that the atomic and ionic radii are of a completely different character; the former are characterised by the distance from the centre of the atom to the maximum electron density of the valence electrons or, since these maxima overlap on formation of the chemical bond, to the maximum density of the electron overlap between the atoms, while the ionic radii are equal to the distance to the electron density minimum in the direction of the bonds between the atoms.

The dependence of the size of the atom on the effective charge can be regarded as semiempirical. For example, for silicon it can be described by the simple expression $r = r_k - 0.05Z^2$, where $r_k$ is the covalent radius and $Z$ the atomic charge. The theoretical values of the orbital radii of $Si^+$ (1.08 Å) and $Si^{2+}$ (0.90 Å) are distributed between the covalent (1.16 Å) and ionic (0.40 Å for a coordination number of 6) radii.[24] It is important to emphasise that the average experimental radius of the silicon ion (0.96 Å), found for silicates, corresponds to a charge of +1.5 e. In its turn the estimated effective charge on the silicon atom agrees closely with the results of the analysis of the distribution of the electron density of silicon discussed above and with numerous data obtained by other physical methods.

Thus the description of the atom as a spherical body for significantly covalent compounds greatly simplifies the radial picture of chemical bonds. The study of the distribution of electron density in various polymorphic modifications of $SiO_2$ is extremely instructive in this sense. In the $SiO_2$ crystal with the rutile structure (stishovite),[77] the chains of $SiO_2$ octahedra having common edges are arranged along the $c$ axis. Each chain is linked to four other chains via oxygen

atoms. It follows from the ionic model that the Si–Si and O–O repulsion in stishovite should lead to a longer Si–O bond directed along the common edge of the octahedra.[77] Experiment has shown that the deformation electron density peaks for the two bonds are respectively 0.47 and 0.30 eÅ$^{-3}$ (Fig. 8*a*) and are somewhat displaced towards oxygen atoms. The distance from them to Si is 1.1 Å, which agrees fairly well with the Slater atomic radius of silicon.[78] The Si–O bonds in the four-membered ring are strained, which is indicated by the shift of the peaks to the outside from the line of the bond (Fig. 8*b*). It is striking that in this plane the peaks are linked by bridges; such distribution of deformation electron density is apparently preferable on energy grounds. In this case the electrons of the bridges shield the nuclei of the cations interacting via the common edge and for this reason, contrary to the ionic model, the corresponding Si–O bonds are shorter.

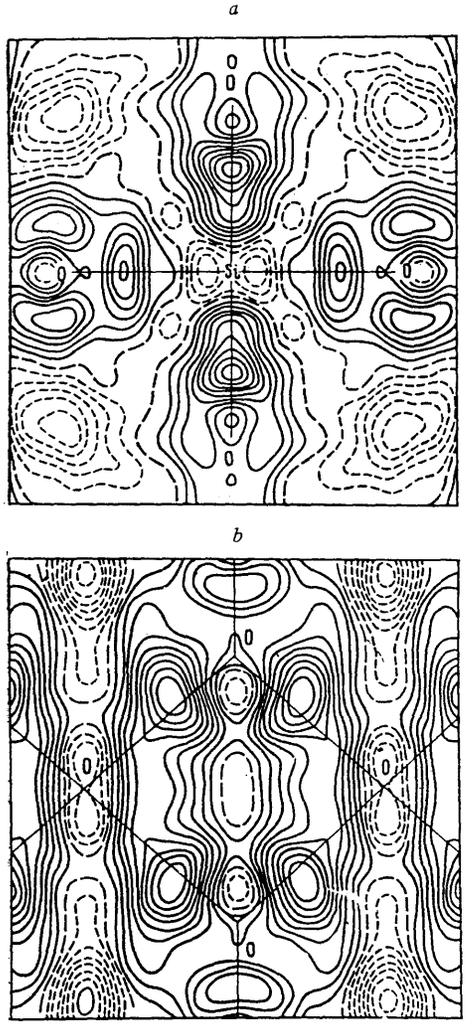



**Figure 8.** Deformation electron density in the stishovite ($SiO_2$) crystal:[72] *a*) section illustrating the non-equivalent Si–O bonds (the Si atom is in the centre); *b*) section through a four-membered ring made up of O atoms; the contour lines are drawn at 0.05 eÅ$^{-3}$ intervals.

As in stishovite, the deformation electron density peaks have been found from the Si–O bonds in α- and β-quartz to one side of the line connecting the atoms.[79] In these $SiO_2$ modifications the deformation of the electron cloud is more complex. We may note the appreciable delocalisation of the electrons along the O–Si–O fragment and the displacement of the centres of gravity of the covalent peaks towards the oxygen atoms. Individual bonds are also linked by bridges, which may be interpreted as evidence for partial double bond character of the Si–O bond. Estimation of the atomic charges by the least squares method using the multipolar expansion showed that the effective charge on silicon in various $SiO_2$ modifications is in the range 1.0–1.7 e, while the charge on oxygen is between −0.5 and −0.85 e.[28] The charge on silicon with a coordination number (C.N.) of 4 is close to 1.0 e and for C.N. = 6 in stishovite it increases to 1.7 e. This indicates an increase of the amount of ionic character of the Si–O bond with increasing C.N. Using the parameter κ, it has been found that the silicon atom in the crystal has contracted while the oxygen atom has expanded relative to the dimensions of the free atoms.

A correlation has been observed experimentally in recent times between the charge on the silicon atom and its coordination number. In particular, it has been found for the compound $K_2Si^{VI}Si_3^{IV}O_9$, where the silicon atoms occupy both tetrahedral and octahedral positions,[80] that the charge on silicon increases with increasing C.N. Refinement of the populations of the valence shells yielded the charges +3.29(15) e for $Si^{VI}$ and +2.52(11) e for $Si^{IV}$, which can be interpreted as an indication of an increase in the amount of ionic character of the bonds in which a Si atom participates as the coordination number of atoms increases.

Estimation of the atomic charges is the simplest method for finding an approximation to the experimental electron distribution. For this purpose, one usually employs either numerical integration of the electron density (for example, for cations over the volume of a sphere whose radius is equal to the radius of optimum separation[27]) or the refinement of the valence electron population of the atoms (as a rule with the aid of the κ technique[18] by the method of least squares). Both methods suffer from a series of disadvantages. Thus the result of the integration depends on the selected volume and that of the refinement procedure on the functions with the aid of which one calculates the scattering amplitude for the valence electrons. Furthermore, the data obtained by these methods agree poorly with one another (Table 6).[81] The estimated values for transition metal atoms in various coordination compounds quoted in Table 6 approach the formal oxidation state only in oxides and silicates (ionic crystals). In organometallic compounds they are appreciably below the formal oxidation states owing to the significant covalent contribution of the metal–ligand bonds. Thus the above estimated charges can hardly be regarded as characteristic of the valence state of the central atom in coordination compounds. More detailed information can be derived from the maps, which make it possible to identify the characteristics of the electronic structure of metal atoms in various crystals.

The study of dinuclear transition metal complexes is of great interest. The character of the chemical bond between the transition metal ions is in this case strikingly different both from the simple picture observed in covalent bonds involving light atoms without d electrons and from the metal–ligand bond. The observed large difference between the lengths of the quadruple M–M bonds (approximately 0.7 Å) shows that the distribution of electron density in various compounds containing such bonds can have significantly different details. The extensive experimental and theoretical studies proved useful for the understanding of the specific

features of these details. The dihydrate of dichromium tetra-acetate $Cr_2(O_2C_2H_3)_4.2H_2O$ has been investigated.[82] In this crystal the moelcule is located at the crystallographic centre of inversion and has an intrinsic $D_{4h}$ symmetry. This made it possible to obtain fairly accurate results by averaging the experimental $\delta\rho$ maps over the chemically equivalent parts of the molecule. According to classical views, a quadruple metal–metal bond is formed in this compound, where the distance between the chromium atoms is 2.36 Å: a single $\sigma$-bond (described by the $d_{z^2}$ orbital), two equivalent $\pi$-bonds ($d_{xz}$ and $d_{yz}$), and a single weak $\delta$-bond ($d_{xy}$) are formed. The contributions of each component differ very greatly in magnitude and the bond order indicated above therefore merely reflects the fact that it can be formally described by four molecular orbitals occupied by eight electrons. The experimental data (Fig.9) show that the deformation electron density in the region of the metal–metal $\sigma$-bond is diffuse and significantly smaller in magnitude than in the Cr–O, C–O, and C–H bonds (approximately 0.1 eÅ$^{-3}$ to within 0.02 eÅ$^{-3}$); on the other hand, somewhat higher peaks (0.12–0.3 eÅ$^{-3}$) are manifested in the region of $\pi$- and $\delta$-bonds. These data agree well with theoretical calculations of the deformation electron density functions for $Cr_2(HCO_2)_4$ in terms of an expanded basis set taking into account configuration interaction.[82] Comparison of the electron populations of the 3*d* orbitals of the free chromium atom (spherically averaged) and the chromium atom in a molecule has shown that the population of the $d_{z^2}$ orbital forming a $\sigma$-bond changes very insignificantly on formation of a molecule and the peaks in the corresponding region are therefore small. The more appreciable change in the populations of other orbitals is accompanied by the appearance of peaks far from the line of the bond. One should note that the 4*s* valence orbital in the molecule is almost unoccupied and this also entails a decrease of the deformation electron density between the metal atoms.

**Table 6.** Charges on transition metal atoms estimated from diffraction data.[81]

| Atom | Atomic charge, e | | Oxidation state | Compound |
|---|---|---|---|---|
| | I | II | | |
| Co | +0.7 (1) | +0.06 (6) | +3 | $[Co(NO_2)_6]^{3-}$ |
| Co | +0.7 (3) | +0.8 (1) | +3 | $[Co(NH_3)_6]^{3+}$ |
| Co | +0.2 (3) | +0.4 (1) | +3 | $[Co(CN)_6]^{3-}$ |
| Cr | +0.15 (12) | — | 0 | $[Cr(Co)_6]$ |
| Cr | +0.1 (1) | +2.78 (6) | +6 | $CrO_4^{2-}$ |
| Co | — | +1.5 (1) | +2 | $CoAl_2O_4$ |
| Mn | +1.58 (1) | — | +2 | MnO |
| Mn | +0.21 (6), +1.49 (6) | — | +2 | $Mn_2SiO_4$ |
| Fe | +0.85 (8), +1.54 (7) | +1.3 (1), +1.9 (1) | +2 | $\alpha$-$Fe_2SiO_4$ |
| Mn | +1.21 (6), +1.49 (6) | +1.3 (1), +2.2 (2) | +2 | $\alpha$-$Mn_2SiO_4$ |

Remarks: The charges quoted in column I were found by the numerical integration of the electron density within the limits of the sphere defined by the optimum separation radius, while column II lists the charges found by the $\kappa$-refinement using the method of least squares.

When configuration interaction was taken into account, it was found[82] that the $\sigma^2\delta^2(\delta^*)^2(\sigma^*)^2$ configuration makes a considerable contribution to the energy of the structure; the contribution of the highly bonding $\sigma^2\pi^4\delta^2$ configuration is only 18%. Thus the antibonding configurations diminish with formal bond order, increasing the bond length.

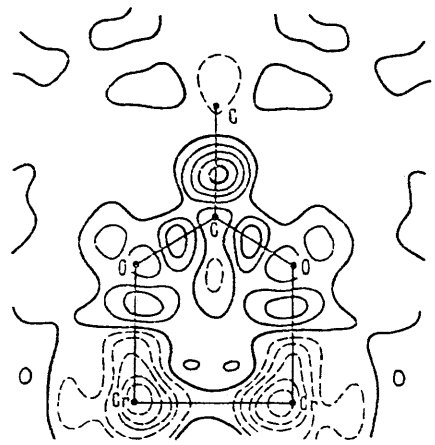



Figure 9. Experimental map of the deformation electron density in the $Cr_2(O_2C_2H_3)_4.2H_2O$ crystal; the section containing the Cr–Cr bond is shown; spacing between lines 0.1 eÅ$^{-3}$.

The characteristic features of the $\delta\rho$ map in $Mo_2(O_2C_2H_3)_4$ in the region of the Mo–Mo bond, whose length is 2.10 Å, are qualitatively similar to the picture described above. However, more intense peaks have been observed[83] between the metal atoms (approximately 0.2 eÅ$^{-3}$) also to one side of the Mo–Mo line (approximately 0.4 eÅ$^{-3}$). Calculated data for the changes in the electron populations of molybdenum[83] suggest that the explanation of the causes of the increase of $\delta\rho$ in the region of the $\pi$- and $\delta$-bonds adduced above in connection with the consideration of $Cr_2(O_2C_2H_3)_4.2H_2O$ is valid also in the case under discussion. Next it was found for $Mo_2(O_2C_2H_3)_4$ that the transfer of electrons from Mo to the neighbouring atoms is accompanied by the appearance of negative minima in the vicinity of the Mo atom on the $\delta\rho$ map in directions corresponding to a decrease of electron density in the antibonding $d_{x^2-y^2}$ orbital. This is characteristic of a transition metal ion in a crystal field with $D_{4h}$ symmetry. It is noteworthy that, in contrast to $Cr_2(O_2C_2H_3)_4.2H_2O$, the contribution of the configuration of the ground state $\sigma^2\pi^4\delta^2$ in this compound is 66% and allowance for the excited configuration hardly alters the deformation electron density map.

The refined features of the electron density in the "ultrashort" quaternary Cr–Cr bond in $[Cr_2(mhp)_4]$, whose length is 1.879 Å at 74 K, have been studied in detail.[84]¶ A $\delta\rho$ peak 0.41 eÅ$^{-3}$ high, extending over the $\pi$- and $\delta$-regions, has been observed between the metal atoms (Fig.10*a*). This peak is so diffuse that it is linked by $\delta\rho$ bridges 0.15 eÅ$^{-3}$ high with the peaks on the metal–ligand

¶ Here mhp = μ-2-hydroxy-6-methylpyridine.

bond. Quantum-chemical calculation for the $Cr_2[H_2P(CH_2)_2]_4$ molecule has shown[84] that the contribution of the δ-component to such a quadruple bond is relatively small and that the σ- and π-interactions play the main role. Negative δρ regions approximately −0.37 eÅ$^{-3}$ deep are directed towards the ligand; this indicates a smaller electron population of the $d_{x^2-y^2}$ orbital compared with the $d_{xy}$ orbital. This is why the $d_{x^2-y^2}$ orbital in fact serves as an acceptor for the unshared electron pairs of the ligands, promoting the formation of a donor–acceptor bond. The theoretical δρ map (Fig. 10*b*), calculated taking into account configuration interaction (the contribution of the $\sigma^2\pi^4\delta^2$ configuration is 55%), agrees well with the experimental map: for example, the height of the peak on the M–M bond is in this case 0.30 eA$^{-3}$. Excess density peaks are observed in both cases when the line of this bond is produced (0.3–0.45 eÅ$^{-3}$), which is caused, according to the authors,[84] by the contraction of the 3*p* and 3*s* shells. Such peaks have also been observed for $Mo_2(O_2C_2R_3)_4$, but could not be interpreted reliably.

Thus experiment has shown that formally identical quadruple metal–metal chemical bonds have, apart from common features, all the characteristic features associated with the specific composition and structure of the compound. This conclusion has been confirmed and supplemented by theoretical calculations. Thus the cases discussed above indicate a tendency towards an increase of the δρ peak located between the metal atoms with decrease of the bond length. On the other hand, the observed small population of the $d_{x^2-y^2}$ orbital changes from compound to compound depending on the nature of the metal atoms and the type of ligand, which alters the ligand–metal–metal angle, changing at the same time the geometry of the compound as a whole. Allowance for the interelectron interaction in binary complexes, which significantly reduces the energy of the system, has different effects on the deformation electron density in various compounds, sometimes leading merely to changes in insignificant details.

In interpreting the deformation electron density maps, one should bear in mind that the construction of difference electron density maps always involves an arbitrary element, because they depend on the choice of the model of the promolecule,[85] which can be made up, in principle, of the electron densities of the free atoms or spherically averaged atoms forming part of the molecule. In the former case the atoms with incompletely occupied *p* and *d* shells have non-zero angular moments and possess a characteristic symmetry. As a consequence of this, differences arise between the electron densities along the chemical bond and at right angles to it and are manifested on the δρ maps. In particular,[85] if the B and C atoms in the ground state are included in the promolecule, then the values of the δρ function along the line of the bond are smaller than in the case where the electron densities of these atoms are spherically averaged. The opposite picture is observed for O and F atoms. For this reason, it is recommended[85] that the promolecule be defined as the set of the electron densities of spherically symmetrical atoms; this reference state has since become generally adopted.

In the calculation of the valence electron density, the separation of electrons into "inner" and "outer" is usually carried out on the grounds of energy considerations. It is then assumed that the densities (and energies) of the "inner" electrons in the molecules and in the free atoms are virtually the same. However, it is known from calculations that, when atoms are involved in a chemical bond, the energies of the inner shells change somewhat.[86] This is also indicated by photoelectron spectroscopic data.[87] Another deficiency of the energy approach to the separation consists in the fact that is is not clear how it can be applied to the electrons of the *s* orbitals located not only in the valence region but also in the vicinity of atomic nuclei.

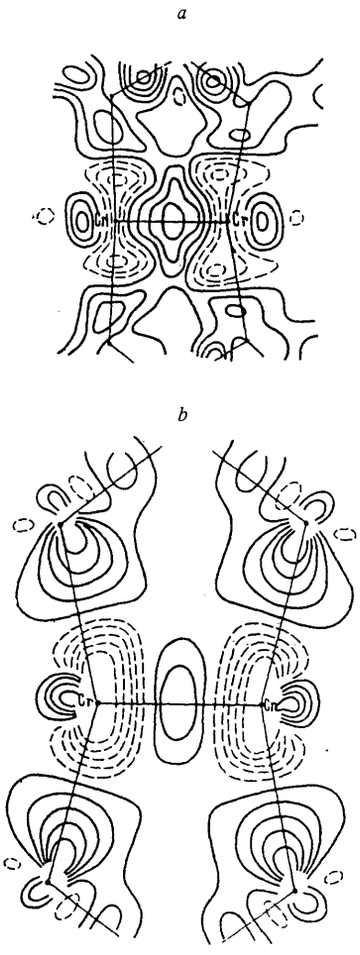



**Figure 10.** Experimental (*a*) and theoretical (*b*) maps of the deformation electron density in the "ultrashort" quadruple Cr–Cr bond;[84] spacing between lines 0.1 eÅ$^{-3}$.

At the same time, it has been noted[88] that points where the radial distribution of the electron density has local minima, whose number is equal to the number of nodes in the radial wave function, exist in atoms. It has been suggested[89] that these minima be regarded as the boundaries between the *K*, *L*, ... layers in the electron shells of atoms. This provides a natural criterion for the subdivision of electrons into skeletal and valence electrons. In molecules the spherical symmetry of the atom breaks down and its electron skeleton is polarised: the skeleton contracts along the bond and expands in a perpendicular direction (dipolar polarisation).[90] However, this polarisation is relatively insensitive to the nature of the other atoms involved in the

chemical bond and the above definition of the skeleton is therefore very suitable for the identification of valence electrons.

Careful analysis[21] made it possible to elucidate the role of the nodes in wave functions in the formation of a chemical bond. An increase of their number in σ orbitals weakens the role of the σ-electron density in the formation of chemical bonds; at the same time the contribution to the electron density described by the π, δ, and other orbitals increases. For this reason, the covalent bonds involving the C, N, and O bonds are apparently stronger than the bonds involving the Si, P, and S atoms.[21]

On the basis of the foregoing, one can conclude that positive peaks on the δρ maps will be manifested in the bonding and non-bonding regions of the molecule and the crystal, while the negative peaks will occur in the regions where the atomic orbitals whose contribution to the molecular orbitals are small are localised. Comparison of the spatial characteristics of the atomic orbitals with the observed electron distribution permits a qualitative interpretation of the latter in terms of the LCAO-MO approximation. Here it is essential to note that the absence of positive δρ peaks in the bonding region does not indicate the absence of a covalent bond. For example, we can imagine a molecular orbital, describing the region of the bond, in the form of a linear combination of the hybrid orbitals of atoms in close proximity each of which supplies one electron to the bond. If these atoms contain more than half-occupied valence shells, then, after spherical averaging, there will be more than one electron per hybrid atomic orbital. In the calculation of the δρ function, this cannot only compensate for the corresponding peaks but can also lead to their negative values in the region of the bond.

Indeed the results of the experimental and theoretical studies have confirmed these considerations. The above picture has been observed, for example, in the N–N bond of diformylhydrazide,[91] the O–O bond in hydrogen peroxide,[92] the C–F bond in tetrafluoroterephthalodinitrile,[93] and also in certain M–M bonds discussed above. We may note the choice of the reference state in a form different from the promolecule (see, for example, Heijser et al.[94]) makes it possible to identify the characteristics of the distribution of the deformation electron density also in such cases, which are difficult to interpret by the standard procedure.

The above refers also to the regions where the unshared electron pairs are located, their peak diminishing and being observed nearer to the centres of the atoms with increase of the electronegativity of the latter.[93] Thus, in the interpretation of the deformation electron density maps, one must take into account the distribution of electrons among the orbitals in the atoms of the promolecule averaged over the orientations.

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It is seen from the data presented that modern diffraction methods make it possible to obtain a clear and detailed picture of the structures of crystalline substances which had been inaccessible hitherto. The new data sometimes agree with the existing crystal-chemical and quantum-chemical views, supplementing and refining them, and sometimes contradict them. At the present time experimental data for a wide range of systems are accumulating rapidly. The electron densities in the fragments of complex biological molecules, medicinal drugs, the organometallic compounds involved in catalytic processes, substances used in instrument making, and minerals are being investigated. A general treatment of these data will enable us to move from qualitative correlations to the establishment of quantitative relations between the electronic structures of substances and their physicochemical properties. So far only the first attempts have been made to seek such relations in the solution of problems concerning complex formation[95] and in the study of materials for non-linear optics;[96] a further development of this approach appears extremely promising.

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# Degree of Charge Transfer in Donor-Acceptor Systems of the $\pi-\pi$ Type

E.Kampar and O.Neilands

The principal methods for the determination of the degree of charge transfer are examined and experimental data on the intermolecular distribution of electron density in charge-transfer complexes and radical-ion salts of the $\pi-\pi$ are surveyed. The relation between the degree of charge transfer and the ionisation potential of the donor, the half-wave potential in the anodic oxidation of the donor, and the electron affinity and the polarographic reduction potential of the acceptor, which largely determine the degree of charge transfer in donor-acceptor systems of the $\pi-\pi$ type, is discussed.
The bibliography includes 104 references.

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## I. INTRODUCTION

The interaction of a π-electron donor with a π-electron acceptor is accompanied by an intermolecular redistribution of electron density. All the properties of the system as a whole depend on the effectiveness of this process, which is characterised by the degree of charge transfer (CT). Weak $\pi-\pi$ complexes exhibit semiconducting and photoconducting properties.[1-3] Systems with a degree of CT within the limits 0.4–0.7 frequently behave as organic metals, while a further increase of the degree of CT again leads to a semiconductur.[6-13] The degree of CT should therefore be regarded as one of the most important characteristics of the donor–acceptor system.

The main textbooks and reviews on donor–acceptor interaction[14-19] include only fragmentary data on the determination of CT in systems of the $\pi-\pi$ type. Theoretical ideas concerning the laws governing the variation of the degree of CT are considered in the present review for the first time and the experimental data on systems of the $\pi-\pi$ type which have accumulated are also discussed.

## II. DEGREE OF CHARGE TRANSFER AND METHODS FOR ITS DETERMINATION

According to Mulliken,[15] the behaviour of a donor–acceptor system can be described by the following wave function:

$$(D, A) \quad (D^+ - A^-)$$

where $\psi_0$ is the wave function of a hypothetical structure in which only the van der Waals interaction obtains and $\psi_1$ the wave function of a hypothetical "dative" structure in which one electron has been transferred from the donor to the acceptor and there is a semipolar bond between the donor and the acceptor, but it need not necessarily be of the localised interatomic type. An increase of the fraction of electron density transferred from the donor to the acceptor corresponds to an increase of the coefficient $b$. The quantitative characteristic of this process is the resulting charge or degree of CT ($\delta$). The degree of CT is expressed[15] as $\delta = b^2 + abS_{01}$, where $S_{01}$ is the overlap integral of the wave functions $\psi_0$ and $\psi_1$. Some workers define the degree of CT as $b^2$ or $b^2/(a^2 + b^2)$,[14] which leads to results in agreement with Mulliken's approach[15] only for very low values of $\delta$.

Thus Mulliken's approach is based on the idea of a partial charge transfer: the real system is assumed to be, as it were, made up of two extreme structures. An analogous interpretation follows from the calculation for the intermolecular complex as a "supermolecule" by the LCAO-MO method.[20-29] As a consequence of the formation of molecular orbitals delocalised over the entire supermolecule, an intermolecular charge distribution takes place and partial resultant charges arise on both the donor and the acceptor. In the determination of this resultant charge, the same difficulties arise as in the determination of atomic charges in calculations for the usual molecules.

A different model is frequently used to describe the properties of crystalline donor–acceptor systems. According to this model, the donor–acceptor system represents a mixture of real donor–acceptor pairs with zero and total charge transfer. The degree of CT or the amount of ionic character is defined as the ratio of the number of pairs with total charge transfer to the total number of donor–acceptor pairs.[6] Although this model differs fundamentally from the previous ones, as regards numerical values it apparently yields the same results as Mulliken's model.

The method of dipole moments, nuclear quadrupole resonance (NQR), X-ray electronic spectroscopy (XES), infrared spectroscopy (IR), Raman spectroscopy (RS), and quantum-chemical calculations are usually employed to determine the degree of CT.[6,14,16,20] The method dipole moments is one of the main ones and has been considered in detail.[16] The dipole moment is a general characteristic of the complex, characterising the charge distribution over the complex as a whole. The experimenqally determined dipole moment of the complex is ususally regarded as the vector sum of the dipole moments of the donor, the acceptor, and the donor–acceptor bond (with a specified geometry of the complex). However, the formation of the complex may be accompanied by a change in the dipole moments of the components and can be also complicated by the formation of complexes of different geometry; this greatly hinders a correct estimation of the dipole moment of the donor–acceptor bond in the study of complexes with a slight degree of CT. The application of the method of dipole moments to the study of weak $\pi-\pi$ complexes is therefore coupled with considerable difficulties.[16,30]

In contrast to the dipole moment method, the NQR method[20] yields information about the local distribution of valence

electrons at the sites where nuclei with a quadrupole moment are located, which must be regarded as a major advantage of the NQR method. However, an exact interpretation of the experimental resonance frequency shifts is not always possible, since the quadrupole interaction constants depend not only on the distribution of valence electrons but also on the contribution by the remaining electrons of the atom involved in resonance, on the degree of hybridisation, on the influence of the crystal field, and on the thermal movement of the molecules. For low degrees of CT, the last effects in fact predominate; analysis of the experimental data obtained in a study of weak $\pi-\pi$ complexes by the NQR method has shown[31] that the influence of the CT on the resonance frequency shift can be fully swamped by the crystal field effects. It is therefore virtually impossible to obtain the quantitative characteristics of the degree of CT for weak complexes by the NQR method.[32]

X-Ray electronic spectroscopy is based on the parallel variation of the effective charges of the atoms investigated and of the shift of their lines in the X-ray electronic spectrum or on the characteristic change in band shape.[33] The principles of the method have been considered in fair detail by Poleshchuk and Maksyutin[20] and Ikemoto et al.[33] One must note that information about the redistribution of valence electrons on complex formation is obtained in this instance from the change in the ionisation potential of the inner electrons, whose ionisation is accompanied by an appreciable reorganisation of the electron shell. Since the decrease of the energy of the ion as a consequence of the reorganisation of the electron shell can exceed by an order of magnitude the change in the ionisation potential due to the redistribution of valence electrons, the interpretation of the experimental data may prove to be very difficult. In practice, this problem is solved by means of a preliminary study of a series of related complexes in which the degree of CT is known beforehand. However, it is clear that the XES method is relatively unsuitable for the study of complexes with an insignificant degree of CT and complications can also arise in the investigation of donor–acceptor systems with a considerable charge transfer.

The IR and Raman spectroscopic methods have not so far found extensive applications in the determination of the degree of CT. IR spectroscopy is used in the study of $\pi-\pi$ complexes as a rule only for the qualitative investigation of the characteristics of the structure of the complex, i.e. it helps to establish whether the intermolecular associated species investigated is a true charge transfer complex (CTC) or a radical-ion salt, whether proton transfer takes place, etc.[14–17,34–40] This is due to the fact that the changes observed in the IR spectra on passing from a weak complex to a radical-ion salt are much more significant than the differences between the spectra of the isolated components and the weak complex or between the spectra of two different weak complexes. However, even the formation of weak $\pi-\pi$ complexes leads to the observation of a number of changes in the spectra,[40] which carry information about the electronic structure of the CTC. Since IR spectroscopy as a method for the determination of the degree of CT has not yet attracted the attention of investigators which it deserves, we believe it necessary to consider in somewhat greater detail the characteristic features of the IR spectra of the CTC.

On formation of the CTC, the following changes may be observed in the IR spectra: the appearance of "forbidden" vibrations of the donor and acceptor and of new vibrations of the donor–acceptor bond and also a spectral shift and a change in the integral intensities of the allowed vibrations of the donor and acceptor.

The appearance of forbidden vibrations of the components in the IR spectrum of the complex is not frequently observed.[41] One of the instances thoroughly investigated in this respect is the CTC of tetracyanoethylene.[42–45] A band appears in the IR spectrum of the hexamethylbenzene–tetracyanoethylene CTC at 1561–1565 $cm^{-1}$, which is due to the $A_{1g}\nu(C=C)$ vibrations of tetracyanoethylene. The study of polarised IR spectra of the CTC single crystal showed that these vibrations are active when the electric field vector of the polarised radiation is directed at right angles to the planes of the donor (D) and acceptor (A) molecules along the alternating DADA stack.[42,45]

This conclusion is satisfactorily consistent with the Ferguson–Person–Friedriech model,[46] which envisages a delocalisation effect on the oscillation of the charge in the direction of charge transfer during vibrations in the plane of the donor or acceptor molecules. In the case of the 2:1 hexamethylbenzene–tetracyanoethylene CTC, two new bands appear in the IR spectrum (at 1567 and 1295 $cm^{-1}$), polarised at right angles to the planes of the donor and acceptor molecules. The latter band refers in all probability to the fully symmetrical vibrations of the $C(CH_3)$ group of hexamethylbenzene. In the spectra of the hexamethylbenzene–hexacyanobenzene, phenanthrene–hexacyanobenzene, and 1,3,5-trimethoxybenzene–hexacyanobenzene complexes, a new band appears at 1300 $cm^{-1}$ and is apparently due to the $A_{1g}\nu(C-C)$ vibrations of hexacyanobenzene, which are manifested in the Raman spectra at 1310 $cm^{-1}$.[47]

Table 1. The shifts of the A bands in the IR or Raman spectra on formation of CTC.

| Donor | Acceptor | $\nu$, $cm^{-1}$ | $\Delta\nu$, $cm^{-1}$ | Assignment | Refs. |
|---|---|---|---|---|---|
| Pyrene | BQ | 1655 | −5 | $\nu_{CO}$ | [50] |
| Hydroquinone | " | 3063 | −1 | $\nu_{CH}$ | [51] |
| " | " | 1654 | −21 | $\nu_{CO}$ | [51] |
| " | " | 3250 | 0 | $\nu^{*}_{OH}$ | [51] |
| " | " | 1357 | −97 | $\nu^{*}_{COH}$ | [51] |
| Hexamethylbenzene | TCNE | 1557 | −5 | $\nu_{CC}$ | [52] |
| " | " | 2228 | −3 | $\nu_{CN}$ | [52] |
| " | " | 1564 | −16 | $\nu_{CC}$ | [53] |
| " | " | 2230 | −7 | $\nu_{CN}$ | [53] |
| *p*-Xylene | " | 1564 | −6 | $\nu_{CC}$ | [53] |
| " | " | 2230 | −7 | $\nu_{CN}$ | [53] |
| Mesitylene | " | 1564 | −4 | $\nu_{CC}$ | [53] |
| " | " | 2230 | −3 | $\nu_{CN}$ | [53] |
| Anisole | " | 1564 | −8 | $\nu_{CC}$ | [53] |
| " | " | 2230 | −3 | $\nu_{CN}$ | [53] |
| *o*-Dimethoxybenzene | " | 1564 | −9 | $\nu_{CC}$ | [53] |
| " | " | 2230 | −3 | $\nu_{CN}$ | [53] |
| Pyrene | " | 2230 | −10 | $\nu_{CN}$ | [53] |
| *o*-Phenylenediamine | TCNQD | 2223 | −13 | $\nu_{CN}$ | [54] |
| Hexamethylbenzene | CA | 1659 | −12 | $\nu_{CO}$ | [55] |
| " | " | 1572 | −11 | $\nu_{CC}$ | [55] |
| " | " | 1112 | −2 | $\nu_{CCl}$ | [55] |
| Pyrene | TNB | 1340 | −5 | $\nu_{NO_2}$ | [56] |
| Anthracene | " | 1546 | −4 | $\nu_{NO_2}$ | [56] |
| " | " | 1360 | −5 | $\nu_{NO_2}$ | [56] |
| Perylene | " | 1546 | −4 | $\nu_{NO_2}$ | [56] |
| Naphthalene | " | 1546 | −6 | $\nu_{NO_2}$ | [56] |
| " | " | 1360 | −8 | $\nu_{NO_2}$ | [56] |
| Hexamethylbenzene | " | 1546 | −6 | $\nu_{NO_2}$ | [56] |
| " | " | 1360 | −9 | $\nu_{NO_2}$ | [56] |
| 1,2-Benzoperylene | " | 1546 | −2 | $\nu_{NO_2}$ | [56] |
| 1,2,5,6-Dibenzanthracene | " | 1546 | −2 | $\nu_{NO_2}$ | [56] |
| Toluene | TCNQD | 2223 | −1 | $\nu_{CN}$ | [57, 58] |
| *o*-Xylene | " | 2223 | −2 | $\nu_{CN}$ | [57, 58] |
| Veratrol | " | 2223 | −2 | $\nu_{CN}$ | [57] |
| 1-Methoxynaphthalene | " | 2223 | −3 | $\nu_{CN}$ | [57] |
| Naphthalene | " | 2223.5 | −3.5 | $\nu_{CN}$ | [58] |
| 2,6-Dimethylnaphthalene | " | 2223.5 | −2.5 | $\nu_{CN}$ | [59] |

Notation: $\nu$ are the frequencies of the vibrations of the corresponding groups in the "free" donor or acceptor; $\Delta\nu$ are the shifts on complex formation. BQ = 1,4-benzoquinone, TCNE = tetracyanoethylene, TCNQD = 7,7,8,8-tetracyanoquinodimethane, TNB = *sym*-trinitrobenzene, and CA = *p*-chloranil.

* Vibrations of the functional groups of the donor; in all the remaining cases the vibrations are those of the corresponding groups of the acceptor.

Few studies have been devoted to the intermolecular D–A vibrations[41] despite the fact that they might yield information about both the strength of the D–A bond and about the degree of CT. This is apparently due to the difficulty of the experimental measurement of absorption bands in the region of 100 $cm^{-1}$ and of the interpretation of the results. For example, a band has been observed at 115 $cm^{-1}$ in the spectrum of the mesitylene–tetracyanoethylene CTC in solution in the donor and was assigned to intermolecular vibrations.[48] Later doubts arose about the correctness of this assignment, since intramolecular vibrations of the acceptor are manifested in this region of the spectrum.[41] More extensive studies on tetracyanoethylene complexes have been carried out by Rossi and Haselbach,[49] who concluded that intermolecular vibrations are indeed observed in the range 80–100 $cm^{-1}$. Both the forbidden vibrations and the D–A vibrations carry information about the degree of CT, but the use of this information for the determination of the degree of CT has not so far been reliably achieved.

Spectral shifts of the allowed absorption bands of the CTC components are almost always observed on formation of crystalline CTC. The magnitude of the shift of the vibrational bands does not then ususally exceed 5–10 $cm^{-1}$ (Table 1) and amounts to more than 20 $cm^{-1}$ only on formation of radical-ion salts.[60]

It is noteworthy that the spectral shift on complex formation has been used by some workers for a kind of classification of donor–acceptor systems. For example, it has been suggested[61] that all the CTC derived from *p*-benzoquinone can be divided into three types depending on the shift of the $\nu$(CO) and $\nu$(CC) stretching vibration bands.

Theoretical ideas about the influence of complex formation on IR spectra have been developed on the basis of several models.[14,15,41,62] At present there is no generally accepted theory taking into account the influence of both the "classical" forces and the CT forces on the spectroscopic parameters of the complex. According to Mulliken's theory,[15] intermolecular charge transfer should be accompanied both by a shift of the allowed bands in the IR spectrum and by a change of their integral intensity. If the band shifts are insignificant, then the relation between $\Delta\nu$ and the degree of CT ($\delta$) is described by the equation:[15,58]

$$\delta = \frac{2\Delta\nu}{\nu_0}\left[1 - \frac{\nu_1^2}{\nu_0^2}\right]^{-1} , \qquad (1)$$

where $\nu_0$ and $\nu_1$ correspond to the positions of the band investigated in the spectra of the "free" component and its radical-ion respectively. It has been shown experimentally that in the case of the TCNQD complexes [there is a shift of the $\nu$(CN) band], for example, Eqn.(1) assumes the following form:[58,59]

$$\delta = 43.5 \cdot \Delta\nu/\nu_0 . \qquad (2)$$

A corresponding equation has been obtained in another study[60] from the experimental band shifts in the spectra of CTC and radical-ion salts with a comparatively high degre of CT known beforehand:

$$\delta = \Delta\nu/44 . \qquad (3)$$

Eqns.(2) and (3) lead to close results, although the degree of CT obtained from Eqn.(2) is lower by 12%. This suggests that the approximation in the form of Eqn.(1) is fairly well-founded and the equation can be used to calculate the degree of CT in other donor–acceptor systems, for example, in a tetracyanoethylene complex.[63] Using the literature data,[64–69] it is possible to obtain equations for the calculation of the degree of CT from the shift of the CO vibration bands in the spectra of the CTC of *p*-benzoquinone and 2,3-dibromo-5,6-dicyano-*p*-benzoquinone:

$$\delta = 11.2 \cdot \Delta\nu/\nu_0 ,$$
$$\delta = 16.6 \cdot \Delta\nu/\nu_0 .$$

The influence of complex formation on the integral intensities of the stretching vibration bands is in the general case more complex.[15] The band intensity is determined by the so-called "$M_{0,1}$ term" which depends both on the change of the dipole moment $\mu_N$ and on the "delocalisation" moment $M_d$, i.e. on the vibronic interactions:

$$M_{0,1} = \partial\mu_N/\partial Q_i + M_d .$$

The quantity $M_d$ may differ from zero if the following parameters change as a consequence of the vibrations investigated: the intermolecular donor–acceptor distance, the ionisation potential, the electron affinity, or the overlap integral $S_{01}$. If the vibrations investigated do not entail such changes, then $M_d = 0$. The term $M_{0,1}$ may be expressed by the dependence on the dipole moments of hypothetical "without bond" and "dative" structures:[15,57]

$$\delta = \frac{A_N^{1/2} - A_0^{1/2}}{A_1^{1/2} - A_0^{1/2}} , \qquad (4)$$

where $A_N$, $A_0$, and $A_1$ are the integral intensities of the stretching vibrations studied in the spectra of the complex, the hypothetical structure "without bond", and the "dative" structure respectively. If one studies, for example, the stretching vibrations of the acceptor, then $A_0$ and $A_1$ should be approximately equal to the integral intensities of the bands due to the given vibrations in the spectra of the "free" acceptor and its radical-anion respectively.[57–59]

It has been suggested[57–59] that Eqn.(4) can be almost always used in the study of the asymmetric vibrations of functional groups in the plane of the donor or acceptor in complexes of the $\pi-\pi$ type, since this should entail virtually no changes in the ionisation potential, the electron affinity, the donor–acceptor distance, and $S_{01}$. The validity of this hypothesis has been confirmed by the results of a study of single crystals of donor–acceptor systems using polarised infrared radiation.[45,55] It was established that the allowed stretching vibrations remain polarised in most cases virtually only in the plane of the component molecules of the CTC; consequently the contribution of the delocalisation moment is indeed insignificant. The stretching vibrations of the CO and CN groups in the CTC of quinones and tetracyanoethylene respectively belong to the above type.[45,55] On the other hand, certain vibrations involving the entire electronic system of the acceptor are polarised also along the DADA stack—for example, the CC vibrations in the 1,4-chloranil molecule (band at 1245 $cm^{-1}$).[45]

A change in the intensities of the bands due to allowed vibrations of the CTC components has been noted in a number of studies and has been used to investigate the CTC of $\sigma$-acceptors.[41] On the other hand, in the case of $\pi-\pi$ complexes the change in the intensities of the allowed vibration bands of the components has so far been used only in a few instances,[56–58,61] although it has been noted in a series of studies that this change is associated with CT from the donor to the acceptor.[45,47,55] It has been established[57] that the change in the integral intensities of the stretching vibration bands of the cyano-groups in the TCNQD spectrum is a more sensitive parameter than the spectral shift and an expression has also been obtained for the calculation of the degree of CT:

$$\delta = \frac{A_N^{1/2} - A_0^{1/2}}{2.8} . \qquad (5)$$

Eqn.(5) has been used to determine the degree of CT in both two-component donor–acceptor systems and in three-com-

ponent donor–acceptor–solvent systems.[57–59] The influence of the universal intermolecular interactions on the spectroscopic properties of the acceptor has been taken into account by studying under the same conditions a model compound which does not form CTC. The data thus obtained agree well with the results secured by other methods.

Among the methods for the determination of the degree of CT, mention should also be made of X-ray diffraction analysis (XDA) and electronic absorption spectra (EAS). The use of the XDA method is based on the characteristic changes in the geometry of the acceptor or donor when a neutral compound is converted into its radical-ion.[70–72] The EAS method is based on the measurement of the integral intensities of the CT bands in the ultraviolet absorption spectra:[14,73–75]

$$b^2 = \frac{f}{1.085 \times 10^{11} h\nu_{CT} R_{DA}^2},$$

where $f$ is the oscillator strength of the electronic transition, $h\nu_{CT}$ the CT energy ($cm^{-1}$), and $R_{DA}$ the intermolecular distance (cm). This equation has been used to determine the degree of CT[14,15,73–75] from the electronic spectra of various complexes in solutions and in the crystalline state (it is essential to take into account the change in $f$ on passing to the crystalline state). The EAS method apparently yields reliable results in the study of CTC with a low degree of CT, for which the energy of the local transitions in the CTC components differs sufficiently from the CT energy.

Electronic spectroscopy can be used to determine the degree of CT from the shfit of the CT band maxima on changing the solvent.[76]

Apart from the methods for the determination of the degree of CT mentioned above, others are also used,[77,78] among which mention should be made of the elastic scattering of neutrons[79] and the measurement of the temperature dependence of the magnetic susceptibility.[80]

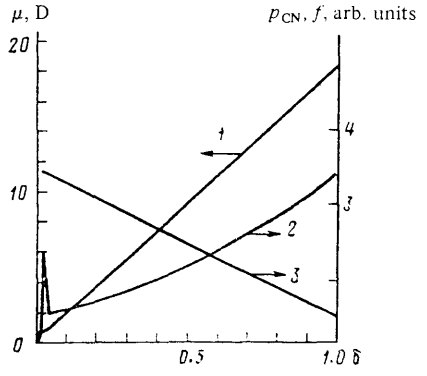



**Figure 1.** The calculated dependence of the dipole moment μ (line *1*), the oscillator strength $f$ (line *2*), and the CN bond order $P_{CN}$ (line *3*) on the degree of CT for model 7,7,8,8-tetracyanoquinodimethane complexes.[21]

The accuracy and reliability of the above methods are fairly difficult to estimate. Nevertheless, the results of calculations for the model complexes of 7,7,8,8-tetracyanoquinodimethane by the LCAO-MO method in the CNDO/S valence approximation give rise to the possibility of such analysis.[21] Fig.1 shows that the results of the calculation confirm the extremely high sensitivity of the dipole moment method. One should note that the $z$ component of the dipole moment (the selected geometry of the complex is characterised by the fact that the donor has been displaced relative to the acceptor along the $C_{2v}$ axis) is directly proportional to the degree of CT throughout the region. The overall dipole moment of the complex may differ from zero also in the absence of CT; one must therefore assume that the dipole moment method can be used with a high degree of accuracy for the study of complexes in which the degree of CT exceeds 0.03. Fig.1 shows that the EAS method based on the measurement of the integral intensities is probably comparatively unreliable. Its application is justified only in those cases where it is known that the transition accompanied by charge transfer does not interact with electronic transitions of another type.

One must assume that IR spectroscopy is a reliable method for the determination of the degree of CT, since, throughout the entire range of variation of the degree of CT, an approximately linear relation is observed between the degree of CT and the order of the bonds formed by the cyano-groups of the acceptor (Fig.1). However, one must note that this method can be used successfully only in those cases where the degree of CT exceeds 0.03, since the bond order hardly changes when δ varies in the range 0.01–0.03.

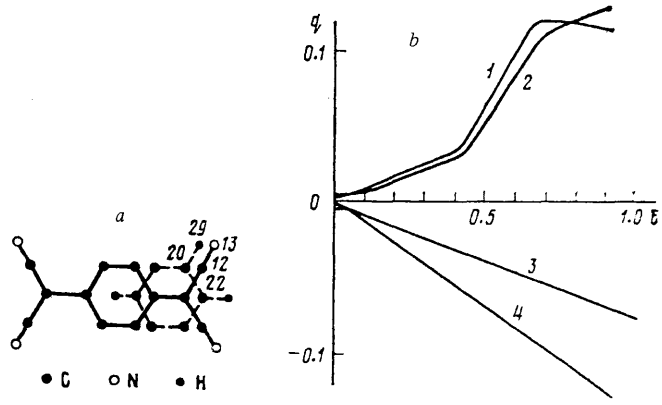



Figure 2. The selected geometry of the complex (*a*) and the dependence of the effective charges $q$ on the individual donor atoms [1) C(20); 2) H(29)] and acceptor atoms [3) N(13); 4) C(7)] (*b*) on the degree of CT for model 7,7,8,8-tetracyanoquinodimethane complexes (calculation by the LCAO-MO method).[21]

Extremely interesting results have been obtained by comparing the degree of CT with changes in charge density on individual atoms of the charge-transfer complex. It was found that the relation between the characteristics investigated is not described in all cases by a simple linear equation (Fig.2). One should also note that in the region of weak CTC ($\delta < 0.05$) the changes in charge density are insignificant and may even prove to be the opposite to those expected [for example, the charge density on the C(22) atom of the donor increases slightly with decrease of δ]. It is therefore clear that all the methods for the determination of the degree of CT based on the measurement of parameters depending on the charge density on individual atoms can be used only for $\delta \geq 0.03–0.05$. The possibility of a non-linear relation between δ and $q$ makes it necessary, in its turn, to treat

the results obtained by these methods with a certain amount of caution at least in those cases where the experimental determination of the above relation has not been carried out for a sufficiently large number of examples in which the degree of CT was known beforehand.

Thus, one must conclude that the dipole moment and IR spectroscopic (and also RS) mrthods are the simplest and most reliable, but apparently there is as yet no reliable method for the determination of the degree of CT for $\delta \leqslant 0.03$.

## III. THEORETICAL IDEAS CONCERNING THE DEPENDENCE OF THE DEGREE OF CHARGE TRANSFER ON THE CHARACTERISTICS OF THE SYSTEM COMPONENTS

Mulliken's theory[15] yields several simple approximate equations describing the dependence of the degree of CT on the difference between the ionisation potential of the donor $I_D$ and the electron affinity of the acceptor $EA$. Among them, mention should be made of the equation

$$\delta^{1/2} \simeq b \simeq \frac{CS_{01}}{I_D - EA - E_c} , \qquad (6)$$

where $C$ is a constant for the CTC of the given type and $E_C$ the energy of the Coulombic interaction of the oppositely charged species in the excited state of the $(D^+, A^-)$ complex ($E_C \cong 3$–$3.3$ eV).

The following expression can also be obtained from Mulliken's theory:[15]

$$\left[\frac{1-\delta}{\delta}\right]^{1/2} \simeq -\frac{1}{\beta_0}(I_D - EA) + \frac{E_c}{\beta_0} , \qquad (7)$$

according to which the comparatively simple function of $\delta$ is approximately linearly related to the difference $I_D - EA$.

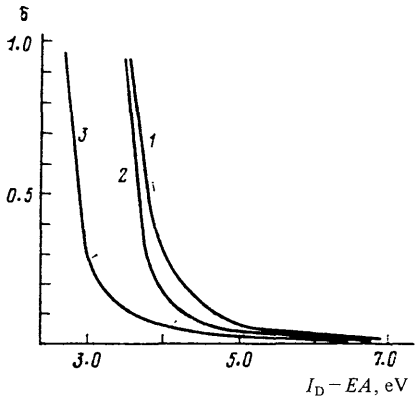



Figure 3. Dependence of the degree of CT on the difference between the ionisation potential of the donor and the electron affinity of the acceptor according to Mulliken's theory [1) $c^2S_{01} = 0.1$, $E_C = 3.2$ eV; 2) $c^2S_{01} = 0.16$, $E_C = 3.2$ eV] and the molecular orbital method in the CNDO/S valence approximation (curve 3).[21]

Although the above equations describe fairly satisfactorily the behaviour of a real system only for a comparatively small degree of charge transfer, they can be used successfully for a preliminary study of the dependence of the degree of CT on the characteristics of the CTC components (Fig.3).

Fig.3 also illustrates a relation obtained in calculations for model complexes,[21] which is represented by a function of the difference between the energies of the frontier molecular orbitals of the complex. Evidently Eqn.(6) and calculations by the LCAO-MO method predict the existence of a range of critical values of the difference $I_D - EA$, in which a comparatively sharp transition from the CTC to the radical-ion state should be observed.

Initially examination of this relation for mixed DADA stacks in the crystalline state[81–83] led to somewhat different results, according to which there exists not a critical region but a critical value of the difference $I_D - EA$ for which an abrupt transition to the radical-ion state should be observed. However, it has been shown[6,84] that a sharp increase of the degree of CT also in the crystalline state takes place likewise over a specific range of values of the above difference (Fig.4). It has been noted[6] that this range is in fact of greatest practical interest.

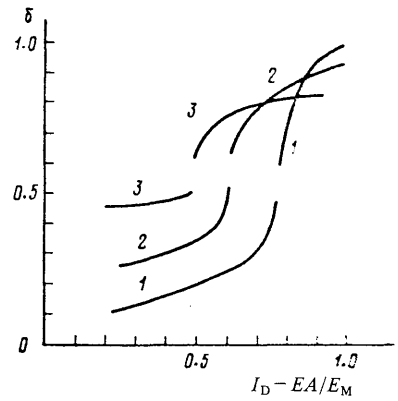



Figure 4. Characteristic form of the dependences of $\delta$ on $I_D - EA/E_M$ for different ratios $\beta/\gamma$ ($\beta$ and $\gamma$ are the resonance and Coulombic integrals respectively): 1) 0.1; 2) 0.3; 3) 0.5.[6]

In crystals consisting of individual alternating stacks of D and A, the degree of CT is also not always unity.[6,83] For the majority of the complexes considered, the state of the system is described by the expression $E(\delta) = E_M(\delta) + (I_D - EA)\delta$, where $E_M$ is the Madelung energy. Other conditions being equal, this should lead to approxomately the same dependence of $\delta$ on the difference $I_D - EA$ as that illustrated in Fig.4.

## IV. EXPERIMENTAL DATA

The majority of the experimental determinations of the degree of CT available at present for donor–acceptor systems of the $\pi$–$\pi$ type both in solutions and in the crystalline state are listed in Table 2. It follows from these data (Fig.5) that the experimental results agree satisfactorily with the theoretical predictions (Fig.3). The fairly considerable scatter of the experimental points is due to the experimental errors in the determination of $I_D$ and $EA$ and also to the approximate nature of the equations (which do not take into account the changes in $S_{01}$, $E_C$, and $E_M$ on passing from one donor–acceptor system to another). Despite this, it is seen

from Fig. 5 that the transition from weak CTC to a state with almost total CT does not take place abruptly but in a certain transition region in the range $3.8 \leqslant I_D - EA \leqslant 4.3$ eV. The region $3.5 \leqslant I_D - EA \leqslant 4.1$ eV corresponds to donor-acceptor systems with the properties of quasi-one-dimensional metals, since these systems are characterised by a considerable but not complete CT.

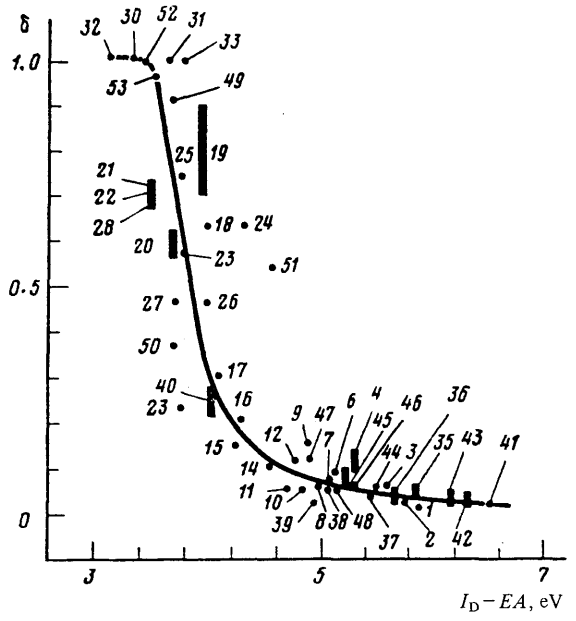



**Figure 5.** Dependence of the experimental values of δ on the difference $I_D - EA$. The ionisation potentials were taken from Refs. 94–97 and the electron affinities from Ref. 98; the numbering of the points corresponds to the numbering of the complexes in Table 2.

Apparently not only electrophysical characteristics but also the crystal structure is controlled in a definite manner by the degree of CT. It has been noted[99] that, on passing from one range of degrers of CT to another, a change in the method of packing is also observed. Indeed, donor–acceptor systems with $0.3 < \delta < 0.7$ consisting of mixed stacks are virtually unknown (according to Kistenmacher,[100] the dibenzotetrathiafulvalene–TCNQD complex is a system of this kind); systems with $\delta < 0.2$ consisting of individual stacks of the donor and acceptor species have not been observed either. All the foregoing findings suggest that the determination of fairly exact relations between the degree of CT and the characteristics of the system components, on the one hand, and between the degree of CT and chemical, spectroscopic, and photo- and electro-physical characteristics of the donor–acceptor systems, on the other, constitutes a branch of the field under consideration whose development will permit the purposeful synthesis of donor–acceptor systems in the future.

The possibility of refining relations of the type $\delta = f(I_D - EA)$ depends in the first place on the accuracy of the determination of $I_D$ and $EA$. Only the ionisation potential can be determined with adequate accuracy at the present time but usually this applies only to the vertical and not the

**Table 2.** The degree of charge transfer in π–π complexes and radical-ion salts.

| No. | Donor | $I_D$, eV | Acceptor | δ | Conditions | Method | Refs. |
|---|---|---|---|---|---|---|---|
| 1 | Toluene | 8.72 | TCNQD | 0.01 | I | IRS | [57] |
| 2 | *o*-Xylene | 8.6 | " | 0.02 | I | " | [57] |
| 3 | Anisole | 8.42 | " | 0.06 | I | " | [57] |
| 4 | Naphthalene | 8.12 | " | 0.08 | II | " | [57] |
| | " | 8.12 | " | 0.13 | III | XDA | [77] |
| 5 | 2-Ethylnaphthalene | 8.0 | " | 0.06 | I | IRS | [57] |
| 6 | Veratrol | 7.99 | " | 0.08 | I | " | [57] |
| 7 | Hexamethylbenzene | 7.95 | " | 0.08 | III | EAS | [74] |
| 8 | 2,6-Dimethylnaphthalene | 7.82 | " | 0.06 | II | IRS | [58] |
| 9 | 1-Methoxynaphthalene | 7.72 | " | 0.15 | I | " | [57] |
| 10 | Acenaphthene | 7.66 | " | 0.05 | III | EAS | [74] |
| 11 | Pyrene | 7.53 | " | 0.05 | III | " | [74] |
| 12 | Carbazole | 7.6 | " | 0.12 | III | " | [74] |
| 13 | *p*-Terphenyl | — | " | 0.16 | III | XDA | [77] |
| 14 | Anthracene | 7.40 | " | 0.105 | III | EAS | [74] |
| 15 | Perylene | 7.12 | " | 0.15 | III | XDA | [85] |
| 16 | Phenothiazine | 7.14 | " | 0.2 | III | " | [74] |
| 17 | Dimethyldihydrophenazine | 6.9 | " | 0.3 | III | " | [77] |
| 18 | *N*-Methylphenazine | 6.8 | " | 0.63 | III | RS | [86] |
| | " | 6.8 | " | 0.63 | III | IRS | [60] |
| | " | 6.8 | " | 0.7 | III | RRS | [87] |
| 19 | Tetramethyl-*p*-phenylenediamine | 6.75 | " | 0.9 | III | XDA | [88–90] |
| 20 | Tetrathiafulvalene | 6.5 | " | 0.59 | III | XES | [88–90] |
| | " | 6.5 | " | 0.59 | III | IRS | [60] |
| | " | 6.5 | " | 0.56 | III | XES | [33] |
| | " | 6.5 | " | 0.59 | III | ENS | [75] |
| | " | 6.5 | " | 0.62 | III | " | [75] |
| | " | 6.5 | " | 0.61 | IV | XDA | [77] |
| 21 | Tetramethyltetrathiafulvalene | 6.3 | " | 0.72 | III | XES | [91] |
| | " | 6.3 | " | 0.63 | III | IRS | [60] |
| 22 | Hexamethylenetetrathiafulvalene | 6.3 | " | 0.72 | III | " | [60] |
| 23 | Tetramethyltetraselenafulvalene | 6.58 | " | 0.57 | III | " | [60] |
| | " | 6.58 | " | 0.21 | III | — | [60] |
| 24 | Tetraselenafulvalene | 7.17 | " | 0.63 | III | IRS | [60] |
| 25 | Hexamethylenetetraselenafulvalene | 6.6 | " | 0.74 | III | " | [60] |
| 26 | Dibenzotetrathiafulvalene | 6.8 | " | 0.46 | III | " | [60] |
| 27 | Diphenyltetrathiafulvalene | 6.55 | " | 0.46 | III | " | [60] |
| 28 | Dimethyltetrathiafulvalene | 6.3 | " | 0.68 | III | " | [60] |
| 29 | Hexamethylenediselenadithiafulvalene | 6.45 | " | 0.72 | III | " | [60] |
| 30 | Tetrathiafulvalene | 6.5 | TFTCNQD | 1.0 | III | " | [60] |
| 31 | Dibenzotetrathiafulvalene | 6.8 | " | 1.0 | III | " | [60] |
| 32 | Hexamethylenetetrathiafulvalene | 6.3 | " | 1.0 | III | " | [60] |
| 33 | Hexamethylenetetraselenafulvalene | 6.6 | " | 1.0 | III | " | [60] |
| 34 | Hydroquinone | 7.95 | BQ | 0.21 | III | XDA | [92] |
| 35 | Durene | 8.3 | CA | 0.04 | II | DM | [14] |
| | " | 8.3 | " | 0.06 | II | EAS | [14] |
| 36 | Naphthalene | 8.12 | " | 0.04 | II | DM | [14] |
| | " | 8.12 | " | 0.02 | II | EAS | [14] |
| 37 | Hexamethylbenzene | 7.95 | " | 0.04 | — | DM | [14] |
| | " | 7.95 | " | 0.04 | II | EAS | [14] |
| 38 | Pyrene | 7.53 | " | 0.06 | II | " | [14] |
| 39 | Anthracene | 7.4 | " | 0.02 | II | " | [14] |
| 40 | Tetrathiafulvalene | 6.5 | " | 0.2 | III | IRS | [93] |
| | " | 6.5 | " | 0.27 | III | XES | [93] |
| 41 | Durene | 8.3 | TNB | 0.02 | II | DM | [14] |
| | " | 8.3 | " | 0.02 | II | EAS | [14] |
| 42 | Naphthalene | 8.12 | " | 0.03 | II | DM | [14] |
| | " | 8.12 | " | 0.02 | II | EAS | [14] |
| 43 | Hexamethylbenzene | 7.95 | " | 0.04 | II | DM | [14] |
| | " | 7.95 | " | 0.03 | II | EAS | [14] |
| 44 | Durene | 8.3 | TCNE | 0.06 | II | DM | [14] |
| 45 | Hexamethylbenzene | 7.95 | " | 0.07 | II | " | [14] |
| | " | 7.95 | " | 0.08 | III | EAS | [73] |
| 46 | Naphthalene | 8.12 | " | 0.06 | III | DM | [14] |
| 47 | Acenaphthene | 7.66 | " | 0.12 | III | EAS | [73] |
| 48 | Dibenzofuran | 7.9 | " | 0.05 | III | " | [73] |
| 49 | Tetrathiafulvalene | 6.5 | 3,3,5,5-tetrachloro-*p*-diphenoquinone | 0.81 | III | XES | [93] |
| 50 | " | 6.5 | 3,3,5,5-tetrabromo-*p*-diphenoquinone | 0.36 | III | " | [93] |
| 51 | " | 6.5 | pyromellitic dianhydride | 0.54 | III | " | [93] |
| 52 | " | 6.5 | 2,3-dichloro-5,6-dicyano-1,4-benzoquinone | 1.0 | III | " | [93] |
| 53 | Tetramethyltetratetrathiafulvalene | 6.3 | TCNE | 0.96 | II | IRS | [63] |

Notation. IRS = Infrared spectroscopy, RS = Raman spectroscopy, RRS = resonance Raman spectroscopy, XES = X-ray electronic spectroscopy, ENS = elastic neutron scattering, and DM = determination of dipole moments; TFTCNQD = tetrafluoro-7,7,8,8-tetracyanoquinodimethane. Conditions in the measurements: I) solution of the donor; II) solution; III) crystalline state; IV) crystalline state at a pressure of 4.6 kbar.

adiabatic ionisation potentials, which would have to be used in the analysis of rules governing the variation of $\delta$. The latest studies in this field have shown[101] that only in the case of aromatic hydrocarbons is the discrepancy between the vertical and adiabatic ionisation potentials small ($\leqslant$0.1 eV). On the other hand, in the case of donors such as tetrathiafulvalenes the discrepancy is considerable (from 0.35 to 0.52 depending on the substituents). As regards electron affinity, the accuracy of its determination is undoubtedly inferior to that of the determination of $I_D$, which, together with the errors in the determination of the values of $\delta$, can lead to an additional distortion of the experimental relation.

Taking into account the factors above, the experimental relation (Fig.5) must be regarded as very satisfactory. One should also note that, in determining this relation, no account was taken of the structural characteristics of the donor and the acceptor which could alter quantities such as both $S_{01}$ and $E_C$ and $E_M$. It may be that some information about the changes in $E_C$ and $E_M$ is contained in an implicit form in characteristics of the donor and acceptor such as the half-wave potential for the anodic oxidation ($E^{ox}_{1/2}$) and the half-wave potential for the polarographic reduction ($E^{red}_{1/2}$), because they contain information about the solvation energies ($E_C$ and $E_M$ depend on the ionic radius and the charge density). Since the quantities $E_{1/2}$ characterise in addition adiabatic processes, the determination of the correlation between $\delta$ and $E^{ox}_{1/2} - E^{red}_{1/2}$ is of undoubted interest.

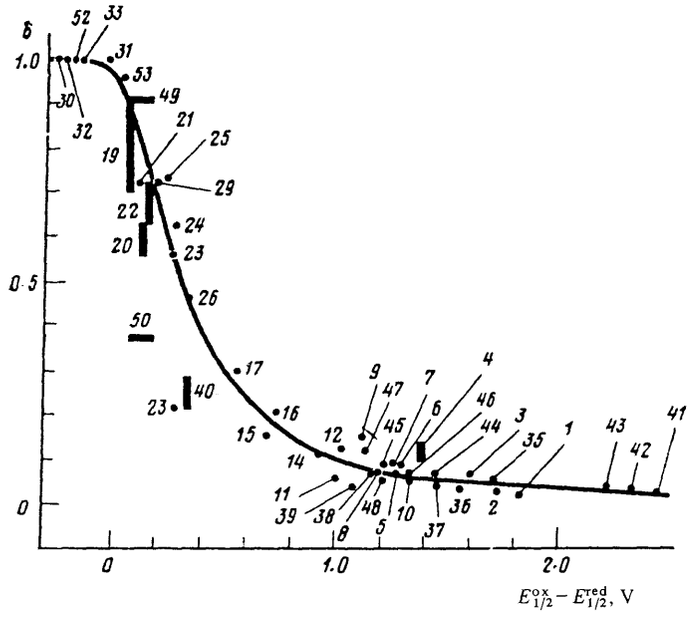



Figure 6. Dependence of the experimental values of $\delta$ on the difference $E^{ox}_{1/2} - E^{red}_{1/2}$. Ther electrochemical characteristics of the components were taken from Refs.10, 98, and 102–104; the numbering of the points corresponds to the numbering of the complexes in Table 2.

It follows from Fig.6 that such a correlation does obtain and that in the region of high degrees of CT it is more pronounced than the relation between $\delta$ and $I_D - EA$. With its aid, it is possible to predict fairly accurately the degree of CT solely from two characteristics of the donor and acceptor which can be comparatively readily determined, namely $E^{ox}_{1/2}$ and $E^{red}_{1/2}$.

It is noteworthy that some scatter in the experimental points is nevertheeless observed. This may indicate the need to take into account also more refined characteristics of the donor–acceptor system, for example, the changes in overlap integrals, etc.

## V. CONCLUSION

The synthesis and investigation of organic complexes and radical-ions with unusual electrophysical characteristics have developed vigorously in recent times. Theoretical ideas permitting the choice of the initial components of the complex for the synthesis of systems having particular properties with a definite reliability have therefore assumed special importance. We believe that the road to these theoretical ideas leads via the determination of a relation between characteristics of the components such as the ionisation potential (the anodic oxidation half-wave potential) and electron affinity (the polarographic reduction half-wave potential) and a characteristic of the complex such as the degree of charge transfer. Here many theoretical and practical problems remain, although the relations obtained already permit a purposeful selection of the components of the complex at a specific level. There is no doubt that, as more accurate methods for the determination of the degree of charge transfer develop and as more extensive experimental data accumulate, relations of the property of the component–property of the complex type will be to a considerable degree refined.

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# Phosphorus Acid Hydrazides

V.M.Ovrutskii and L.D.Protsenko

The review is devoted to the methods of synthesis, chemical reactions, and physicochemical properties of phosphorus acid hydrazides, among which biologically active substances have been discovered.
The bibliography includes 106 references.

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III. Chemical and physicochemical properties 347

## I. INTRODUCTION

The studies in the field of phosphorus acid hydrazides, which began to attract the attention of investigators as early as the end of the past century, have developed particularly vigorously during the last two decades. The presence of two nucleophilic nitrogen atoms together with the nucleophilic phosphorus atom in phosphorus acid hydrazides have led to extensive synthetic possibilities of these compounds. Substances with properties useful in practice have been discovered among phosphorus acid hydrazides. The hydrazides of phosphorothioic acid esters exhibit a pesticidal activity.[1-3] The dihydrazides of halogenophenol esters of phosphorothioic acid and the sulphonyl hydrazides of phosphorothioic acid have been used as bactericides and fungicides.[4,5] Certain hydrazides of phosphoramidothioic acid have been shown to exhibit a weak acaricidal and fungicidal activity.[6] Among phosphorus acid hydrazides, substances with insecticidal activity have been found.[7] The hydrazides of diarylphosphinic acids and esters of methylphosphonic and methylphosphonothioic acid have been synthesised as potential biologically active substances with cytostatic, insecticidal, and pesticidal properties.[8-10]

It has been shown that the hydrochlorides of *O*-aryl-*NN*-di(2-chloroethyl)phosphoramidohydrazidates have a pronounced antitumour activity[11,12] and act selectively in the absence of inhibition of blood generation. Some of the compounds mentioned have shown a high antitumour activity not inferior to that of chlorobutyne.[13,14] Thus the need to search for substances with antitumour activity among phosphorus acid hydrazides by the structural modelling of "carriers" of cytotoxic groups in order to increase the selectivity of the antitumour activity of the compounds has been demonstrated.

Hitherto there have been no reviews of phosphorus acid hydrazides. Bearing in mind that phosphorus acid hydrazides are of both theoretical and practical interest for research, we thought it useful to write the present review of literature data concerning the methods of synthesis and chemical and physicochemical properties of the given class of organophosphorus compounds. The review covers the literature up to the beginning of 1983.

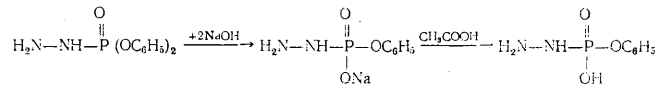
## II. METHODS OF SYNTHESIS

### 1. Hydrazides of Phosphoric Acid

Among all the known phosphorus hydrazides, the largest group comprises the hydrazides of phosphoric acid. These include the hydrazides of phosphoric acid monoesters and diesters, phosphoramidate esters, phosphorodiamidic acids, the dihydrazides of phosphoric esters and phosphoramidic acids, and phosphoric trihydrazides.

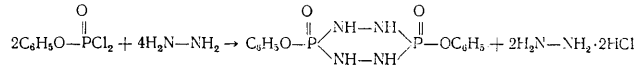
#### *(a) The Hydrazides and Dihydrazides of Phosphoric Acid Monoesters*

One of the methods of synthesis of the hydrazides of monoaryl and monoalkyl phosphate esters involves the partial hydrolysis of the hydrazide of the corresponding phosphoric acid diesters on heating with concentrated solutions of sodium hydroxide or ammonia,[15,16] for example:

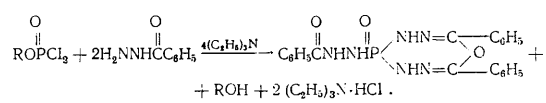


The catalytic hydrogenation of diphenyl phosphorohydrazidate in the presence of platinum dioxide also results in the formation of monophenyl phosphorohydrazidate.[17]

Phenyl phosphorodihydrazidate has been obtained by treating phosphoryl chloride with a calculated amount of phenol and then with hydrazine hydrate in alcoholic solution.[16] *o*-Biphenylyl and *p*-cumenylphenyl phosphorodihydrazidates have been synthesised similarly.[18] The reaction of phenyl phosphorodichloridate with anhydrous hydrazine in ethereal solution also affords only the dihydrazide when hydrazine is used in excess.[16] On reaction with two moles of hydrazine in an aqueous medium, the above acid dichloride gives rise to 3,6-dioxo-3,6-diphenoxy-1,2,4,5,3,6-tetra-azadiphosphane:[19,20]

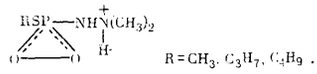


A study of the reaction of alkyl (and aryl) phosphorodichloridates with benzoylhydrazine in the presence of triethylamine showed that its product is 3-benzoylhydrazido--3-oxo-6,8-diphenyl-3-phospha-7-oxa-1,2,4,5-tetra-aza-cyclo-octa-5,8-diene:[21]



Interesting data have been obtained in a study of the reaction between *S*-alkyl phosphorodichloridothioates and 1,1-dimethylhydrazine.[22] *S*-Alkyl-2,2-dimethylphosphorohydrazidates were isolated in 26–40% yield and were found to exhibit unusual acid–base properties. Their basic

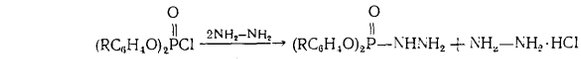
properties proved to be very weak ($pK_a < 2$) and so were their acid properties. The $pK_a$ in water were 5.22 ± 0.05 for R = $CH_3$ and $C_3H_7$. On the basis of these properties and IR and $^1H$ NMR spectroscopic data, it has been suggested that the above compounds exist in the form of the dipolar ions:



R = $CH_3$, $C_3H_7$, $C_5H_9$ .

*(b) Hydrazides and Substituted Hydrazides of Phosphoric Acid Diesters*

The most widely used method of synthesis of the hydrazides of phosphoric acid diesters involves the reaction of the corresponding chlorides of phosphoric acid diesters with hydrazine, hydrazine hydrate, or substituted hydrazines. The reaction can also be carried out in the presence of water, using sodium carbonate to bind the hydrogen chloride evolved. Diaryl phosphorohydrazidates have been obtained in this way: [16,23,24]



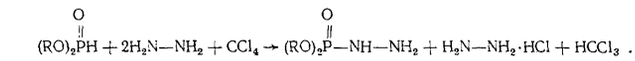
The phosphorylation of hydrazine, *NN*-dimethylhydrazine, phenylhydrazine, and acetylhydrazine by alkyl 2-chlorophenyl phosphorochloridates has been studied and it has been established that, when the reaction is carried out in benzene solution and the reactants are in molar proportions of 1 : 2, then the monohydrazides of the mixed phosphoric acid diesters are produced. [25]

It is of interest that the nature of the hydrazine hardly influences the rate of reaction, since the basicity of substituted hydrazines changes insignificantly, in contrast to the amines.

The reaction of hydrazine with 2-chlorophenyl ethyl phosphorochloridate yielded, together with the monohydrazide, also the *NN*-bishydrazide as a side product. The amount of the bishydrazide increases when anhydrous hydrazine is used.

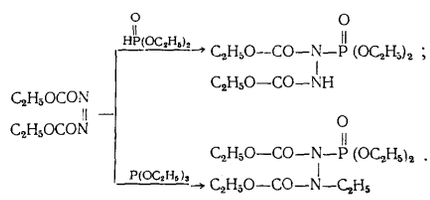
1-Alkyl-substituted hydrazides of phosphorus acids have been described for the first time by Shanduk et al., [23] in particular diaryl phosphoro(1-ethylhydrazidates) $(C_6H_5O)_2$.
O
‖
.$PN(C_2H_5)NH_2$. The 1-substitution of the resulting hydrazide has been confirmed by its ability to form the corresponding hydrazones with *p*-nitrobenzaldehyde.

Dialkyl phosphorohydrazidates can be obtained by the Todd–Atherton reaction by treating dialkyl phosphites with two moles of hydrazine and carbon tetrachloride: [16,26]



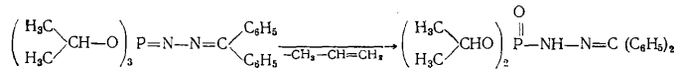
A modification of the Todd–Atherton method, based on the use of anhydrous potassium carbonate as the base in the presence of the phase transfer catalyst $(C_2H_5)_3\overset{+}{N}CH_2C_6H_5Cl^-$ in the reactions of dialkyl phosphites with hydrazine hydrate and carbon tetrachloride. [27]

Dialkyl or trialkyl phosphites react with azo-compounds to form the corresponding dialkyl phosphorohydrazidates: [28]

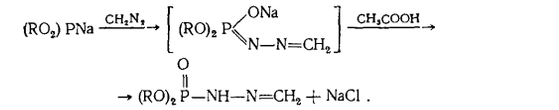


Dialkyl phosphorohydrazidates can be obtained also by reducing dialkyl azophosphoric acids with various reductants. [29]

The thermal decomposition of trialkoxyphosphazines at 170–180 °C is accompanied by the elimination of propene and the formation of di-isopropyl phosphoro(2-diphenylmethylenehydrazidate): [30]



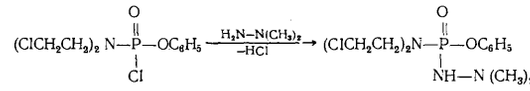
The salts of dialkyl phosphorous acids react with diazomethane to form dialkyl phosphoro(2-methylenehydrazidates): [31]



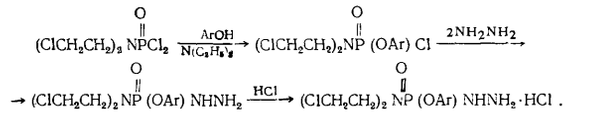
A communication about the synthesis of diethyl phosphoro(diphenylhydrazidates), which have been little investigated, has been published recently. [32]

*(c) Hydrazides of Phosphoramidate Esters*

There are comparatively few literature data on the hydrazides of phosphoramidate esters. Phenyl phosphoro[di(2-chloroethyl)amido](2,2-dimethylhydrazidate), formed when phenyl phosphoro[di(2-chloroethyl)amido]chloridate reacts with dimethylhydrazine, has been described: [33]

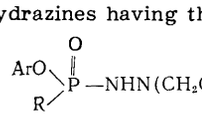


A method of synthesis of the hydrochlorides of aryl phosphoro[*NN*-di(2-chloroethyl)amido]hydrazidates, consisting in the reaction of aryl phosphoro[*NN*-di(2-chloroethyl)amido]-chloridates with hydrazine in a mixture of anhydrous benzene and methanol and subsequent bubbling of a benzene solution with hydrogen chloride, has been developed: [34]



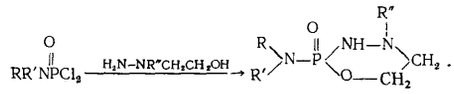
It has been established that the reaction between aryl phosphoro[*NN*-di(2-chloroethyl)amido]chloridates and phenylhydrazine proceeds in benzene in the presence of triethylamine with formation of the corresponding phenylhydrazides. [34]

The reaction between substituted phosphoromonochloridates and di(2-chloroethyl)hydrazine has been investigated and phosphorylated hydrazines having the formula



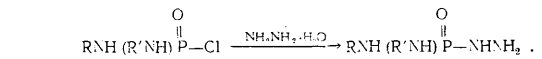
where R is a tetra-acetylglucose residue, were synthesised for the first time. [35]

Cyclic hydrazides of phosphoramidate esters, formed from phosphoramidic dichlorides and the corresponding substituted hydrazines, are known: [36]



*(d) Hydrazides and Dihydrazides of Phosphoramidic Acids*

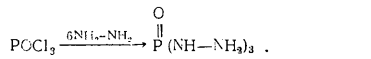
A preparative method for the synthesis of phosphorodiamidic hydrazides involves the interaction of the corresponding phosphorodiamidic chlorides with hydrazine hydrate in solution in benzene, dioxan, or tetrahydrofuran at 60 °C:[24,37]



There are comparatively few literature data on phosphoramidic dihydrazides. The synthesis of phosphoramidic dihydrazides from the corresponding phosphoramidic dichlorides and phenylhydrazine has been described.[38]

*(e) Phosphoric Trihydrazides*

Phosphoryl trihydrazides can be obtained by treating phosphoryl chloride with six moles of hydrazine:[16]



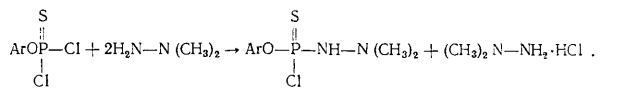
Phosphoryl chloride reacts analogously with six moles of arylhydrazines (phenyl- or 4-methylphenyl-hydrazine) in solution in ether or chloroform. The corresponding phosphoric tris(*N*-arylhydrazides) were isolated in these reactions.[39,40]

## 2. Hydrazides of Phosphorothioic Acid

Among the hydrazides of phosphorothioic acid, the dihydrazides of phosphorothioic esters and hydrazides of phosphorothioic diesters have been most thoroughly investigated.

*(a) The Hydrazides and Dihydrazides of Phosphorothioic Esters*

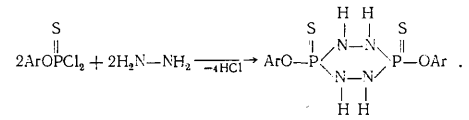
The reaction of *N*-mono- or *NN*-di-substituted hydrazines (*N*-phenyl or *NN*-dimethylhydrazines) with aryl phosphorodichloridothioates, involving the selective substitution of only one chlorine atom and the formation of the corresponding aryl phosphorochloridohydrazidothioates, has been described:[41]



When unsubstituted hydrazine was used under the conditions of this reaction (room temperature or a temperature below 0 °C, two moles of the corresponding hydrazine), the required monohydrazide could not be obtained.

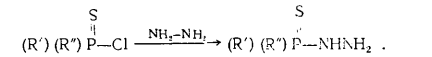
Analysis of the literature data concerning the effect of hydrazines on aryl (and alkyl) phosphorodichloridothioates shows that the nature of the products formed under these conditions depends on the electronic and steric effects, the basicity of the nucleophiles, the reaction temperature, the reactant ratio, and the order in which the reactants are added.

Thus data have been published[41,42] on the synthesis of aryl phosphorodihydrazidothioates by treating one mole of the corresponding phosphorodichloridothioate ester with four moles of hydrazine hydrate, phenylhydrazine, or 1,1-dimethylhydrazine. Phenyl phosphorodihydrazidothioate has been obtained similarly.[16] On the other hand, the formation of a cyclic product, namely 3,6-diphenoxy-3,6-dithiono-1,2,4,5,3,6-tetra-azadiphosphene by the reaction of phenyl phosphorodichloridothioate with two or three moles of hydrazine has been demonstrated:[43]

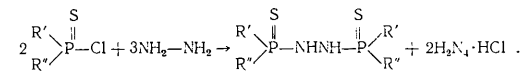


*(b) Hydrazides and Substituted Hydrazides of Phosphorothioic Diesters*

Diaryl (or dialkyl) phosphorochloridothioates, hydrazine, or a substituted hydrazine are used to synthesise the hydrazides of phosphorothioic diesters:



In certain cases the above reaction leads to the formation of secondary hydrazides:



The reaction may be controlled by the polar effects of the groups R′ and R″. Thus the reaction of diaryl phosphorochloridothioates with hydrazine hydrate always affords a high yield of primary hydrazides for an equimolar reactant ratio.[42,44]

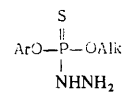
The formation of primary hydrazides from diaryl phosphorochloridothioates and hydrazine hydrate has been established also when the latter was used in excess.[23]

Dialkyl phosphorochloridothioates give rise to not only primary but also secondary hydrazides. The maximum yield of the latter of the type $[(R'O)(R''O)P(S)NH]_2$ is attained when anhydrous hydrazine is added to the corresponding acid monochloride in molar proportions of 3 : 2.

The most convenient method of synthesis of dialkyl phosphorohydrazidothioates is based on the reaction of dialkyl phosphorochloridothioates with two moles of hydrazine hydrate or a substituted hydrazine.[45–47]

The reaction leading to the synthesis of secondary hydrazides becomes more effective with increase of the electron-donating capacity of the substituents R′ and R″. It has been established that, when the sum of the constants ($\Sigma\sigma^*$) of the polar substituents R′ and R″ is greater than +4 (in the presence of aryl substituents), the above reaction does not occur. When $\Sigma\sigma^* = +1$, which happens for the secondary hydrazine $[(CH_3O)_2P(S)NH]_2$, the formation reaction leading to secondary hydrazides proceeds more rapidly and incorporates two bimolecular $S_N$ reactions. In the first of these the corresponding dialkyl phosphorochloridothioates and hydrazine react to form a primary hydrazide. In the second reaction the above intermediate primary hydrazide is phosphorylated with formation of a secondary hydrazide.[47]

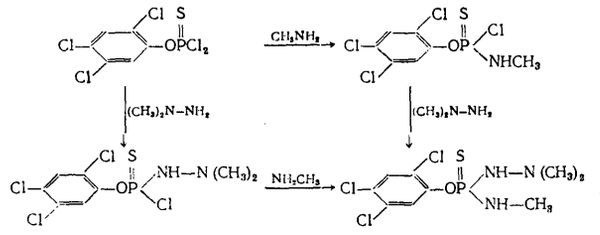
Mixed diesters of phosphorohydrazidothioic acid, formed from the corresponding phosphorochloridothioates and hydrazine hydrate and having the structure



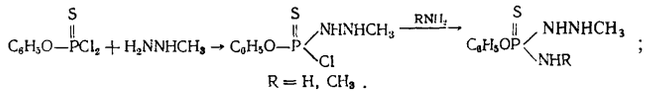
are known.[1,25]

*(c) Hydrazides of Phosphoramidothioic Acid Esters*

Phenyl phosphoramidohydrazidothioates can be obtained by the reaction of 2,4,5-trichlorophenyl phosphorochloridohydrazidothioate or phosphorochlorido(1,1-dimethylhydrazido)thioate with the corresponding amine or by the reaction of, for example, 2,4,5-trichlorophenyl phosphoro(*N*-methylamido)chloridothioate with the corresponding hydrazine.[41,47]



The first method of synthesis of phosphoramidohydrazidothioates has also been described[48] in connection with the synthesis of the following phenyl phosphoramidohydrazidothioates:

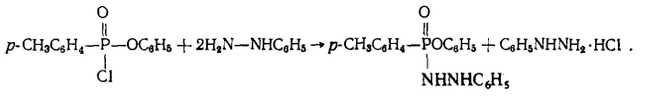


A series of phosphoramidohydrazidothioates have been synthesised by treating alkyl phosphoramidochloridothioates with dimethylhydrazine in boiling benzene in the presence of triethylamine.[6]

## 3. Hydrazides of Phosphonic and Phosphonothioic Acids

*(a) Hydrazides of Phosphonic and Phosphonothioic Acid Esters*

The hydrazides of phosphonic and phosphonothioic acid esters are usually formed when the chlorides of the corresponding acid esters react with hydrazine or a substituted hydrazine. Thus phenyl *p*-tolylphosphonochloridate reacts with phenylhydrazine to form the corresponding phenylhydrazide:[49]

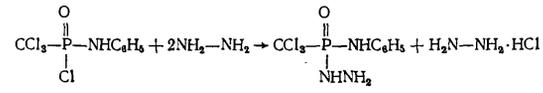


When methyl phosphonochloridate and methylphosphonochloridothioate are added to an excess of hydrazine or hydrazine hydrate, the hydrazides of the above acid esters are formed. When the order in which the reactants are mixed was altered, bisphosphorylated hydrazines were isolated.[9]

The phosphorylation of hydrazine by 2-chlorophenyl methylphosphonochloridate or methylphosphonochloridothioate in proportions of 2 : 1 led to the formation of the corresponding monohydrazide.[25] Aryl methylphosphonochloridates and methylphosphonochloridothioates also react with hydrazine hydrate to form monohydrazides, but, in order to facilitate their isolation, it is necessary to treat the reaction mixture with potassium carbonate.[10]

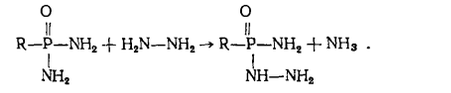
*(b) The Hydrazides of Phosphonamidic Acids*

The usual method of synthesis of phosphonamidic acid hydrazides involves the interaction of phosphonamidochloridates with hydrazine or its derivatives, for example:[50]



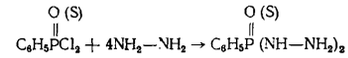
Solutions of strong inorganic bases can also be used to remove the hydrogen chloride formed.

It is of interest that treatment of phosphonic diamides with hydrazine also leads to the formation of phosphonamidic hydrazides:[51]

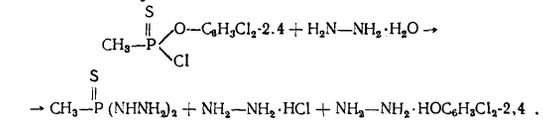


*(c) Dihydrazides of Phosphonic and Phosphonothioic Acids*

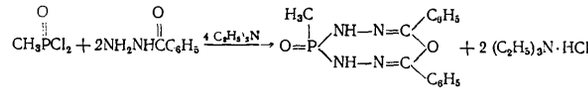
One of the methods of synthesis of the dihydrazides of phosphonic or phosphonothioic acids involves the treatment of the dichlorides of the corresponding acids with hydrazine, for example:[51]



A novel method of synthesis of methylphosphonothioic dihydrazides has also been described.[52] It was found that the interaction of hydrazine hydrate with 2,4-dichlorophenyl methylphosphonochloridate entails the hydrazinolysis of not only the acid chloride but also of the labile ester linkage with formation of a dihydrazide:



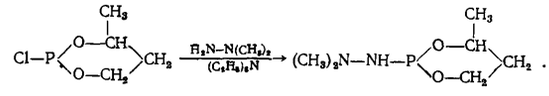
The reaction of methylphosphonic dichloride with two moles of benzoyl hydrazide and four moles of triethylamine in solution in toluene takes place in an unusual manner. The formation of 3-methyl-3-oxo-6,8-diphenyl-3-phospha-7-oxa-1,2,4,5-tetra-azacyclo-octa-5,8-diene was demonstrated in this instance:[53]



The reaction proved to be general for the synthesis of 3-alkyl(aryl)-3-oxo-6,8-diphenyl-3-phospha-7-oxa-1,2,4,5-tetra-aza-cyclo-octa-5,8-dienes.

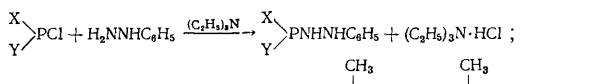
## 4. The Hydrazides of Phosphorous Acid

The first representative of the hydrazides of phosphorous acid was described by Nifant'ev in 1964.[54] It was obtained by the reaction of 1,3-butylene phosphorochloridite with 1,1-dimethylhydrazine in the presence of triethylamine:



The methods of synthesis of the hydrazides of phosphorous acid were investigated in detail in later studies.[55,56] It was

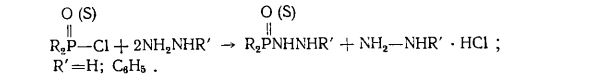
found that the hydrazides can be obtained from the corresponding acid chlorides and phenylhydrazine in the presence of triethylamine as the hydrogen chloride acceptor:



X = Y = $OC_2H_5$; $OC_3H_7$; $OC_4H_9$; —O $(CH_2)_2$O—; —OCHCH$_3$O—; —OCH $(CH_2)_2$O— .

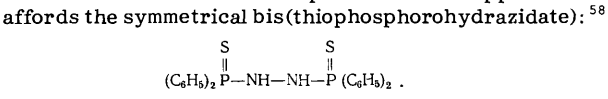
### 5. The Hydrazides of Phosphinic, Phosphinothioic, Phosphinous, and Phosphinothious Acids

The hydrazides of phosphinic and phosphinothioic acids have been synthesised by the reaction of the corresponding acid chlorides with two moles of hydrazine or a substituted hydrazine in an inert solvent: [57]

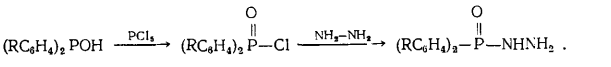


R′=H; $C_6H_5$ .

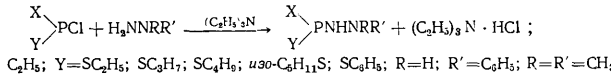
Diphenylphosphinothioic acid hydrazide has been synthesised by adding the chloride of the above acid to hydrazine hydrate. The addition of the components in the opposite order affords the symmetrical bis(thiophosphorohydrazidate): [58]



The hydrazides of diarylphosphinic acids containing both identical and different aromatic substituents at the phosphorus atom have been described. [23] They have been synthesised in accordance with the following schemes:

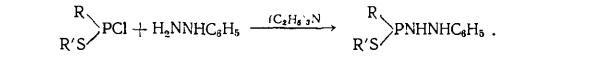


The hydrazides of phosphinous acids, obtained from the corresponding acid chlorides and phenylhydrazine or 1,1-dimethylhydrazine in the presence of triethylamine, are known: [56]



X=$CH_3$, $C_2H_5$; Y=$SC_2H_5$; $SC_3H_7$; $SC_4H_9$; *изо*-$C_6H_{11}S$; $SC_6H_5$; R=H; R′=$C_6H_5$; R=R′=$CH_2$.

2-Phenylhydrazides of alkylphosphinothious acids are formed analogous to the phenylhydrazides of dialkyl phosphorous acids: [59]



The properties characteristic of compounds with a tervalent phosphorus atom are also typical for the hydrazides of phosphinous and phosphinothious acids: they readily combine with elemental sulphur and with copper monohalide salts.

## III. CHEMICAL AND PHYSICOCHEMICAL PROPERTIES

Extensive data characterising the chemical properties of phosphorus acid hydrazides have now accumulated. The presence of nitrogen atoms together with the nucleophilic phosphorus atom leads to the manifestation of amphoteric properties by the above compounds.

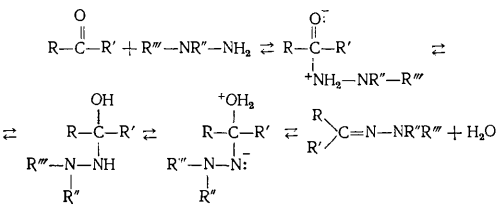
*N*-Unsubstituted hydrazides of phosphorus acids exhibit properties characteristic of other hydrazine derivatives by virtue of the presence of the free amino-group. Firstly, they undergo numerous reactions with electrophiles (aldehydes and ketones, diketones, β-ketoesters, monosaccharides, Schiff bases, carboxylic acids, carboxylic acid chlorides, alkyl chlorocarbonates, chlorides of alkane(arene)-sulphonic acids, phosphorus acid chlorides, picryl chloride, isocyanates, and isothiocyanates). Secondly, they react with nucleophiles (ethanol, phosphoric acids, water, caustic alkalies, and inorganic acids). In addition oxidation reactions are characteristic of phosphorus acid hydrazides.

### 1. Reactions with Electrophiles

#### *(a) Interaction with Aldehydes and Ketones*

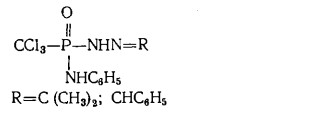
Analysis of the literature data on the interaction of phosphorus acid hydrazides with aldehydes and ketones shows that they can involve both $NNH_2$ and NNH groups.

If the nucleophilic centre of the attacking nucleophile is a nitrogen atom linked to two hydrogen atoms, the reactions with aldehydes and ketones proceed in accordance with the following scheme:



Ultimately the carbonyl group is substituted by the C=NNR″R‴ group, while the intermediate stages involve the highly mobile tautomeric equilibria shown in the scheme above. Acid catalysts accelerate the first stage as a result of the formation of conjugate acids, which polarises the carbonyl group still further. [60,61]

The aldehyde and ketone hydrazones derived from trichloromethylphosphono(*N*-phenylamidic) hydrazides have been described. [50]



The hydrazones derived from phosphoramidates, synthesised from both aliphatic and aromatic aldehydes and ketones, have been described. [24,62]

The following compounds have been used [24] to synthesise the hydrazones: formaldehyde, acetone, ethyl methyl ketone, methyl propyl ketone, acetaldehyde, propioaldehyde, acetophenone, 3,4-dichlorobenzaldehyde, 2-nitrobenzaldehyde, 4-dimethylaminobenzaldehyde, 4-chlorobenzaldehyde, etc.

The reactions of the hydrochlorides of aryl phosphoro[*NN*-di(2-chloroethyl)amido]hydrazidates with formaldehyde, benzaldehyde, and acetophenone have been investigated. [62,63] The reactions were carried out with heating in an alcoholic medium, without isolating the phosphoramidohydrazidate base, with formation of aryl phosphoro[*NN*-di(2-chloroethyl)-amido][2-alkylidene(arylalkylidene)hydrazidates].

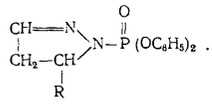
Kitaev and co-workers [64,65] established that the arylhydrazones can exist in aqueous-methanolic solutions in three tautomeric forms.

Ovrutskii et al. [66] used polarography at a dropping mercury electrode for the first time to investigate the tautomeric transformations of aryl phosphoro[*NN*-di(2-chloroethyl)-amido](2-methylene, benzylidene-, and methylbenzylidene-hydrazidates). The investigation showed that the half-wave potentials of the hydrazo-group in these phosphoroalkylidene-(arylalkylidene)hydrazidates differ little and remain constant

when the solutions of the test compounds are kept for a long time. This factor as well as the finding that half-wave potentials ranging from −0.6 to −0.96 V correspond to the azo-forms of the aldehyde and ketone arylhydrazones, while half-wave potentials ranging from −1.34 to −1.56 V have been obtained for the hydrazones derived from the above phosphorohydrazidates at pH 5.8 and 9.2, suggest that these hydrazones do not undergo reversible transformations under the polarographic conditions and do not have the structure of the azo-form but are in fact true hydrazones.

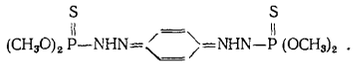
The influence of various substituents in the aromatic ring on the polarographic reduction has been estimated quantitatively. The quantities $\rho^*$ at pH 5.8 and 9.2 are 0.25 and 0.20 respectively ($r = 0.99$; $S = \pm 0.2$). The constant $\rho^*$ for the reduction of the C=N group at pH 5.8 and 9.2 is virtually invariant, which indicates the absence of changes in the mechanism of reduction at a dropping mercury electrode.

It is of interest that, when unsaturated aldehydes and ketones (acrolein and crotonaldehyde) are used in the reaction with diphenyl phosphorohydrazidate, five-membered heterocycles, namely pyrazolines, are formed:[56,67]

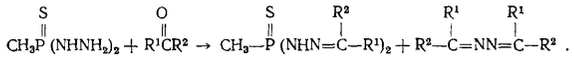


Diphenyl phosphoro(2-dimethylmethylenehydrazido)thioate has been obtained by the reaction of diphenyl phosphorohydrazidothioate with acetone.[25]

The reaction of dialkyl phosphorohydrazidothioates with aldehydes and ketones lead to the formation of the corresponding hydrazones derived from the phosphorothioic acids,[47,68] while the reactions with benzoquinone afford the compound



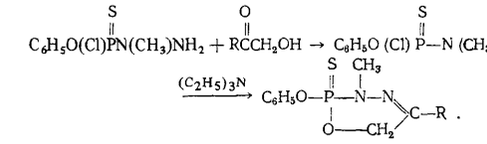
Grapov and co-workers[69] were the first to investigate the reactions of the dihydrazides of phosphorothioic acids with aldehydes and ketones and established that methylphosphonothioic dihydrazide reacts with benzaldehyde, *p*-chlorobenzaldehyde, *o*-, *m*-, and *p*-nitrobenzaldehydes, and *p*-dimethylaminobenzaldehydes to form the corresponding dihydrazones derived from methylphosphonothioic acids. Aldazans were isolated as side products. The reactions with acetone and acetophenone yielded the dihydrazones:



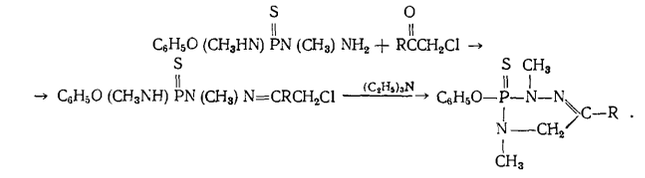
At the same time the reaction of methylphosphonothioic dihydrazide with benzophenone led to the isolation of only tetraphenylketazine.

The bisbenzylidenehydrazones derived from methylphosphonothioic acid have also been synthesised by the reaction of benzaldehyde and its substituted derivatives with methylphosphonothioic dihydrazide in the presence of acetic acid in an alcoholic medium as the catalyst.[52]

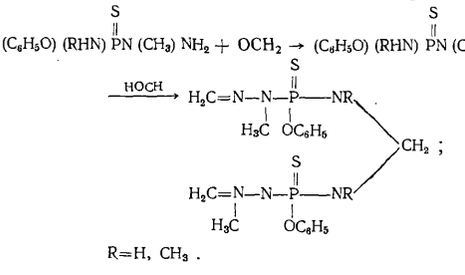
Interesting data have been obtained in the study of the reactions of asymmetric *N*-methylhydrazides of phosphorus acid with aldehydes and ketones.[48] Thus phenyl phosphorochlorido(1-methylhydrazido)thioate reacts with aldehydes and ketones to form hydrazones, which are converted in the presence of triethylamine into the corresponding 3-methyl-2-phenoxy-2-thiono-1,3,4,2-oxadiazaphosphorines:



1,3-Dimethyl-2-phenoxy-2-thiono-1,3,4,2-triazaphosphorines have been obtained by treating phenyl phosphoro(*N*-methylamido)(1-methylhydrazido)thioate with various ketones in the presence of triethylamine:

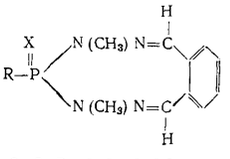


Treatment of phenyl phosphoro(*N*-alkylamido)(1-methylhydrazido)thioates with an excess of formaldehyde results in a reaction in accordance with the following mechanism:



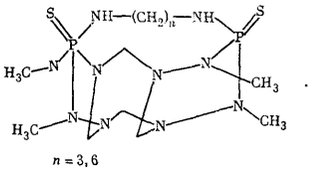
R=H, $CH_3$.

Di(1-methylhydrazides) of phosphoric, phosphonic, phosphorothioic, and phosphonothioic acids react with phthalic dialdehyde to form the dihydrazones:



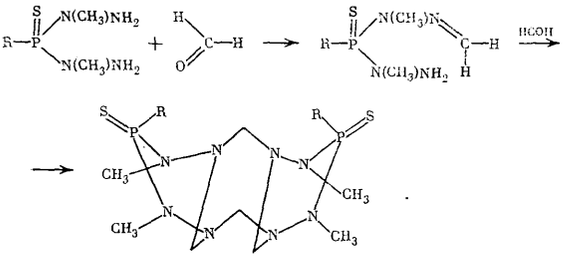
X=O; S; R=$C_6H_5$; $C_6H_5O$.

The tetra(1-methylhydrazides) $(H_2NCH_3N)_2\overset{S}{\overset{\|}{P}}NH(CH_2)_nNH\overset{S}{\overset{\|}{P}}.(NCH_3NH_2)_2$ react with formaldehyde to form the compounds



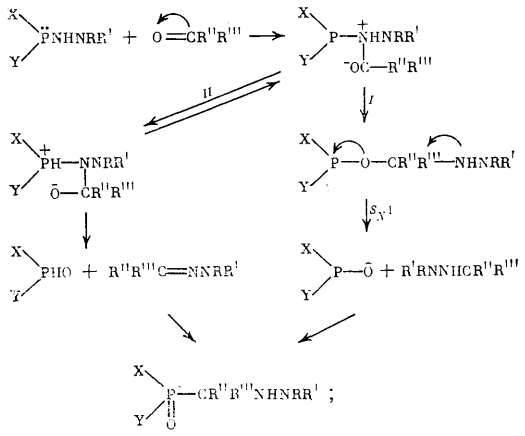
$n = 3, 6$

Treatment of the asymmetric phosphorodi(1-methylhydrazido)-thioate with one mole of formaldehyde leads to the corresponding perhydro-1,2,4,5-tetra-azaphosphorines, which react with formaldehyde to form tetracyclic compounds:



The structure of these compounds has been demonstrated by $^{1}H$ and $^{31}P$ NMR, IR and UV spectroscopy, and mass spectrometry.

The interaction of phosphorus acid hydrazides containing the NNH group with aldehydes and ketones has been investigated.[56,70] The reaction of dialkyl phosphoro(2-phenylhydrazidites) and *S*-alkyl alkylphosphono(2-phenylhydrazido)thioites with aldehydes and ketones yielded α-hydrazinophosphinates [and phosphonates?]. A reaction mechanism involving the formation of a four-membered ring as a result of the attack by the nucleophilic nitrogen atom on the electrophilic carbon atom of the carbonyl group, similar to that of the Staudinger–Wittig reaction, has been proposed:

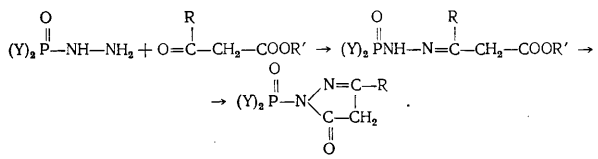


*I*: X=Y=$OC_2H_5$; $OC_3H_7$; $OC_4H_9$; —O $(CH_2)_2$ O—;
—OCH($CH_3$) $(CH_2)_2$ O—; —OCH($CH_3$) $(CH_2)_2$ O—; R=H; R′=$C_6H_5$;
*II*: X=$CH_3$; $C_2H_5$; Y=$SC_2H_5$; $SC_4H_9$; $SC_3H_7$;
neo-$C_5H_{11}$S; R=H; R′=$C_6H_5$; R=R′=$CH_3$; R″=$C_3H_7$; R‴=H; R″=$C_4H_9$; R‴=$C_2H_5$.

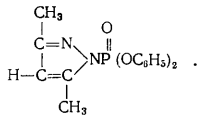
It is suggested that the initial intermediate can rearrange, as in case I, to produce an α-hydrazinophosphinite, which then rapidly decomposes via an $S_N1$ mechanism to form the final product. There is also a possibility of a proton shift (case II) with formation of a phosphonobetaine and the subsequent final stage of the Staudinger–Wittig reaction.

### *(b) Interaction with β-Ketoesters and α- and β-Diketones*

Ketoesters react with diphenylphosphinic hydrazide and diphenyl phosphorohydrazidate to form the corresponding hydrazones, which split off the alcohol on heating in solution to form phosphorylated pyrazolones:[56,67,71]

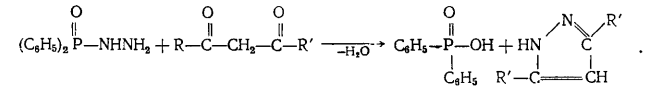


The use of acetylacetone instead of acetoacetic ester in the above reaction leads to the formation of 1-diphenoxyphosphoryl-3,5-dimethylpyrazole.[67]

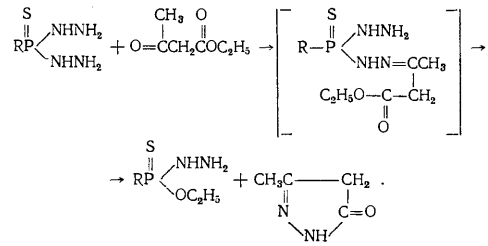


According to the data of Jahns et al.,[72] the reaction of diphenylphosphinic hydrazide with acetylacetone in equimolar proportions yielded 3,5-dimethyloxopyrazolyl diphenylphosphinate. Its structure was demonstrated by a specific synthesis from 3,5-dimethylpyrazole and diphenylphosphinic acid. After the reactions with benzoylacetone and dibenzoylmethane, only the corresponding hydrazones were isolated.

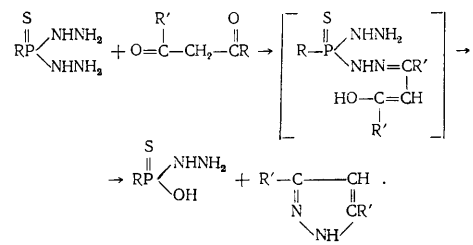
The reaction of diphenylphosphinic hydrazide with acetylacetone in proportions of 2 : 1 gave a 50% yield of an adduct from which diphenylphosphinic acid and 3,5-dimethylpyrazole were isolated after hydrolysis:



The reactions of the dihydrazides of various phosphorothioic acids with β-ketoesters and α-diketones have been studied in fair detail.[69] The reactions of phosphorodihydrazidothioic acids and phosphonothioic dihydrazides with acetoacetic ester proceed on heating in alcohol with dissociation of the P—N bond and the formation of 3-methylpyrazolone and ethyl phosphorohydrazidate and phosphonohydrazidothioate respectively:

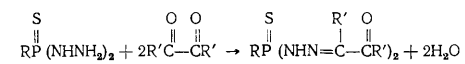


Methyl(phenyl)phosphonothioic dihydrazides and phosphorodihydrazidothioic acids react with acetylacetone and dibenzoylmethane to form respectively 3,5-dimethylpyrazole and 3,5-diphenylpyrazole. In addition, a hydrazidoacid is apparently formed, but its stability is low and the authors were unable to isolate it in a pure form:



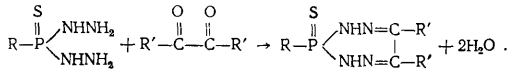
The interaction of dihydrazides of methylphosphonothioic and a number of other phosphorus thioacids with α-diketones (diacetyl and dibenzoyl) proceeds in different ways depending on the reactant ratio.

The reaction of one mole of methylphosphonothioic dihydrazide or phosphorodihydrazidothioic acid with two moles of α-diketone in alcohol at 50–60 °C affords a high yield of phosphonothioic di(2-acetylalkylidenehydrazide) or (2-benzoylbenzylidenehydrazide) (or the corresponding phosphorothioate):



The dihydrazides of methyl- and phenyl-phosphonothioic acids and ethyl and phenyl phosphorodihydrazidothioates react with α-diketones or glyoxal in proportions of 1 : 1 to give 3-thiono-3,1,2,4,5-phosphatetra-azacyclohepta-5,7-

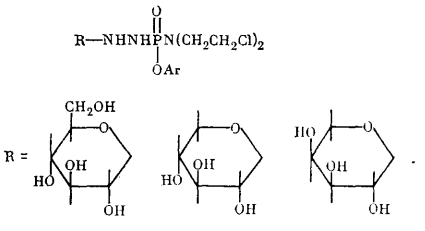
dienes:



Thus the structure of the products of the reactions of phosphorus acid hydrazides with β-ketoesters and diketones depends on the nature of the substituents in the carbonyl and hydrazone residues and on the nature of the initial reactants. The hydrazone cyclisation reactions with formation of a pyrazoline ring take place at the instant of the formation of the hydrazones or on heating the latter in solution and take place either with the dissociation of the P–N bond or with its retention.

*(c) Interaction with Monosaccharides*

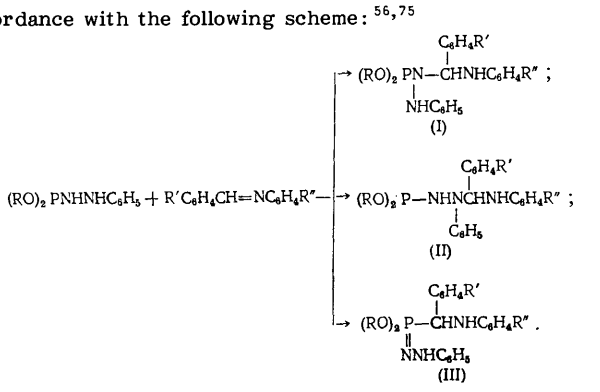
The interaction of phosphorus acid hydrazides with monosaccharides has been investigated in recent years.[73] The corresponding [*O*-aryl-*NN*-di(2-chloroethyl)amidophosphoryl]-hydrazo-derivatives of D-glucose, D-xylose, and L-arabinose having the following formulae were obtained:



The IR spectra of these derivatives were investigated and it was established that the shift of the band characteristic of the OH group can be accounted for by the formation of an intramolecular hydrogen bond characteristic of the ring ($\nu$ = 3420–3380 cm$^{-1}$). The hypothesis of a cyclic structure of monosaccharides is also confirmed by the data characteristic of the antisymmetric vibrations of the pyranose ring ($\nu$ = 930–920 cm$^{-1}$). It has been shown that the products of the interaction of phosphorus acid hydrazides with D-glucose and D-xylose show deformation vibrations due to the equatorial position of the C–H bond relative to the pyranose ring ($\nu$ = 840–835 cm$^{-1}$), while in the case of the products of the interaction of phosphorus acids with L-arabinose, deformation vibrations of the C–H bond corresponding to the axial position of the hydrogen atom ($\nu$ = 900 cm$^{-1}$) were found. The bands in the range 1680–1600 cm$^{-1}$, characteristic of the hydrazone C=N group, are missing from the spectra of all the compounds.[74] The data obtained permit the conclusion that in the free crystalline states the compound synthesised do not exist as the true hydrazones (derivatives of the acyclic forms) but are in fact derivatives of the cyclic pyranose forms.

*(d) Interaction with Schiff Bases*

The reactions of the 2-phenylhydrazides of phosphonous acids with Schiff bases have been investigated. The reaction can involve both the NH groups of the phenylhydrazide and the phosphorus atom, i.e. can proceed with or without the transfer of the reaction centre and can give adducts in accordance with the following scheme:[56,75]



The properties of the products isolated from the reaction mixture (they do not combine with elemental sulphur and their hydrolysis gives rise to a phenylhydrazine salt) correspond to the structure of the product of the addition of the Schiff base to the phosphorus atom (structure III).

Ethylene phosphoro(1-phenylhydrazidites) react with Schiff bases to form the corresponding ethylene (α-anilino)-benzyl-*N*-anilinophosphazines.

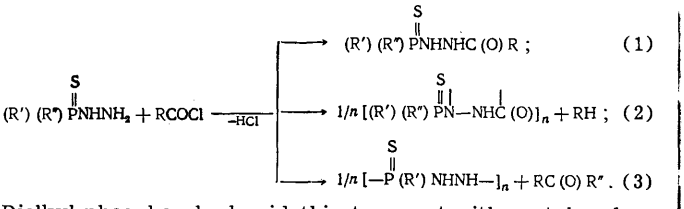
*(e) Interaction with Carboxylic Acids*

The interaction of diethyl, dibutyl, ethylene, and propylene phosphoro(2-phenylhydrazidites) with carboxylic acids (acetic, propionic, and butyric) is of the type of a double decomposition reaction with formation of carboxylic acid hydrazides and the corresponding phosphorus acids.[76]

The reactions of dialkyl and alkylene phosphoro(2-phenylhydrazidites) with acrylic or methacrylic acid proceeds with formation of phosphorous acid and probably with the initial formation of the hydrazide of an unsaturated acid, which cyclises to the corresponding pyrazolidinone or pyrazolone. 1-Phenyl-5-pyrazolidinone, 1-phenyl-5-pyrazolone, 4-methyl-1-phenyl-5-pyrazolidinone, and 4-methyl-1-phenyl-5-pyrazolone were obtained.

*(f) Interaction with Carboxylic Acid Chlorides, Alkyl Chlorocarbonates, Alkane(arene)sulphonic Acid Chlorides, and Phosphorus Acid Chlorides*

The monohydrazides of phosphorus acids readily react with carboxylic acid chlorides to form acyl derivatives. The pathway followed in the reactions of phosphoric (phosphorothioic) hydrazide derivatives with acyl chlorides, benzoyl chloride, and ethyl chlorocarbonate depends on the structure of the derivatives of the phosphorus acid hydrazides and also on the electrophile:[47]

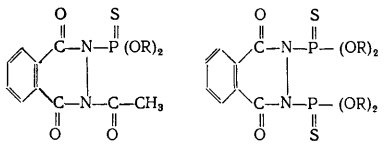


Dialkyl phosphorohydrazidothioates react with acetyl and benzoyl chlorides to form *N*-thiophosphoryl-*N'*-acylhydrazides [via reaction (1)].

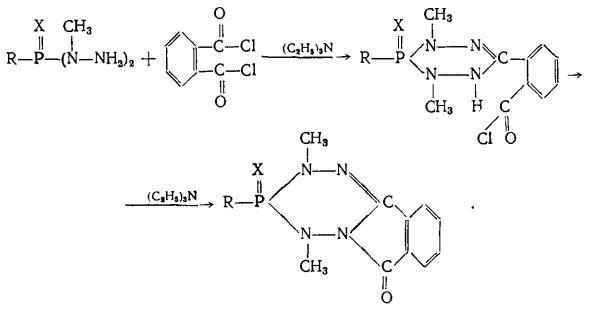
The reaction of phosphorodi(*N*-methylamidic) hydrazide with acetyl chloride leads to the formation of *NN*-dimethylacetamide and a condensed phosphorohydrazidate system [via reaction (3)].

*NNN'*-Triacyl-*N*-thiophosphoryl hydrazides and *NNN'*-triacetyl-*N*-dialkoxythiophosphoryl hydrazides have also been described.[47]

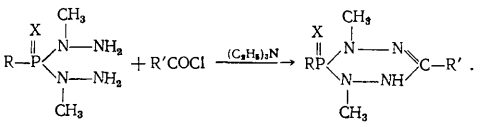
When phthaloyl chloride was allowed to react with *N*-acetyl-*N*-dialkoxythiophosphoryl hydrazides and *NN'*-bis(dialkoxythiophosphoryl) hydrazides, 3-acetyl-2-dialkoxythiophosphoryl-1,4-phthalazinediones and 2,3-bis(dialkoxythiophosphoryl)-1,4-phthalazinediones were obtained.[47]



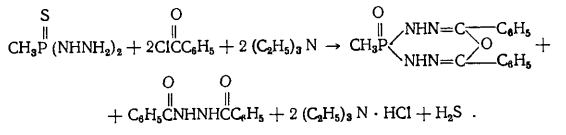
The di(1-methyl)hydrazides of phosphorus acids react with phthaloyl chlorides in the presence of triethylamine via the mechanism[48]



The interaction of di(1-methyl)hydrazides of phosphorus acids with formyl, acetyl, and benzoyl chlorides has been investigated. The reaction proceeds via the mechanism[48]

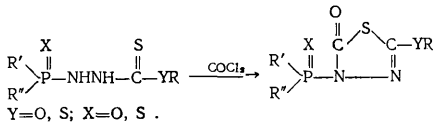


The acylation of methylphosphonothioic dihydrazide[69] with 2 moles of benzoyl chloride leads to the formation of 3-phospha-7-oxa-1,2,4,5-tetra-azacyclo-octa-5,8-diene:

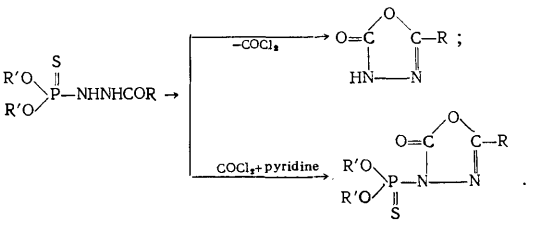


Sulphur is evolved in this reaction in the form of hydrogen sulphide.

The reactions of *N*-alkoxy(alkylthio)thiocarbonyl hydrazides of dialkyl phosphoric (phosphorothioic, phosphonothioic) acids with phosgene yielded the corresponding phosphorylated thiadiazoles:[77]

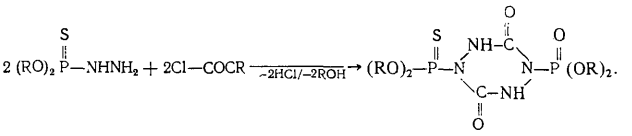


When dialkyl phosphorohydrazidothioates are treated with phosgene, the P—N bond is retained or broken depending on the reaction conditions. When the reaction is carried out in pyridine, phosphorylated oxadiazoles are formed. If the reaction proceeds in the presence of phosgene alone, the P—N bond is broken with formation of the phosphorothioic acid residue and oxadiazoles:

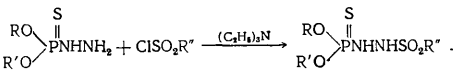


The reactions of phosphorus acid hydrazides with alkyl chlorocarbonates yielded aryl phosphoro[*NN*-di(2-chloroethyl)amido[(2-ethoxycarbonylhydrazidates),[62] diphenyl phosphoro(2-ethoxycarbonylhydrazidates),[78] and phosphorodi(*NN*-alkylphenylamidic) 2-methoxy(ethoxy)carbonylhydrazides.[79]

When dialkyl phosphorohydrazidothioates are treated with ethyl chlorocarbonate in the presence of alkaline reagents and in an inert organic solvent, 1,4-di(alkoxythiophosphoryl)-3,6-dioxo-1,2,4,5-tetrazines are formed in accordance with the mechanism[47,68]



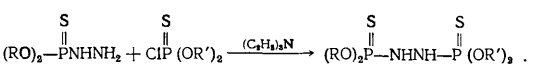
The reactions of phosphorohydrazidothioate esters with alkane (arene)sulphonyl chlorides take place in organic solvents in the presence of triethylamine with formation of 2-sulphonylhydrazides:[80,81]



The syntheses of phosphoramido(2-sulphonylhydrazido)-thioic acid and phosphorodi(*NN*-dialkylamido)thioic 2-sulphonylhydrazides,[5,82] aryl phosphoro[*NN*-di(2-chloroethyl)amido[(2-methanesulphonylhydrazidates),[62] aryl phosphoro[*NN*-di(2-chloroethylamido](2-*p*-toluenesulphonylhydrazidates),[63] phosphorodi(*NN*-alkylphenylamidic)-2-toluene-*p*-sulphonylhydrazides,[71] and phosphorodi[β-alkane-(arene)sulphonylhydrazido]thioic acids[83] have also been achieved.

The reaction of diphenyl phosphorohydrazidate with diphenyl phosphorochloridate leads to the formation of *NN'*-bis(diphenoxyphosphoryl)hydrazide.[16]

Bis(1,2-thiophosphoryl)hydrazides with various substituents at both phosphorus atoms have been obtained in the presence of triethylamine:[47,84,85]

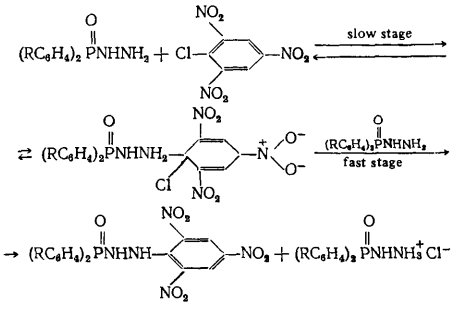


The formation of bis(1,2-dialkoxythiophosphoryl)hydrazide by the reaction of dialkyl phosphorohydrazidothioate with dialkyl phosphorochloridothioate has been described.[8,16,50]

### *(g) Interaction with Picryl Chloride*

Diarylphosphinic hydrazides have been synthesised, the kinetics of their reactions with picryl chloride have been investigated, and a mechanism has been proposed for this

reaction:[8]

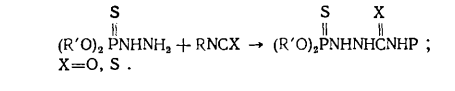



The reaction kinetics are described by a second-order equation, which is demonstrated by the linear time variation of the reciprocal of the current concentration. The reaction investigated obeys the Arrhenius equation. The activation energy $E_a$, the frequency factor $\lg A$, and the activation entropy have been calculated. It has been shown that the reactivity of diphenylphosphonic acid in the reaction with picryl chloride increases after the introduction of electron-donating substituents and diminishes in the presence of electron-accepting substituents.

*(h) Interaction with Isocyanates and Isothiocyanates*

Numerous studies have been made on the mechanism and kinetics of the reactions of phosphorus acid hydrazides with isocyanates and isothiocyanates.[47,86–94]

The interaction of dialkyl phosphorohydrazidothioates with isocyanates and isothiocyanates was first described by Tolkmith[47,86] and takes place in accordance with the mechanism presented below with formation of the corresponding semicarbazides and thiosemicarbazides:




Diphenylphosphinylthiosemicarbazides[87] and 4-acetyl-1-diphenylphosphinylthiosemicarbazides[88] are known.

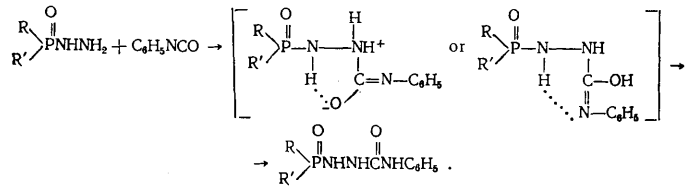
β-Phosphorylated semicarbazides and thiosemicarbazides are formed on interaction of aryl methylphosphonohydrazidates and methylphosphonohydrazidothioates and ethylphosphono(*NN*-diethylamido)thioic hydrazide with alkyl and aryl isocyanates and alkyl and aryl isothiocyanates.[89]

Phosphonohydrazidic acids react more readily with isocyanates than phosphonohydrazidothioic acids. In the former case the reactions proceed in the absence of a catalyst, while in the latter catalytic amounts of triethylamine are required. In the series of isothiocyanates only aryl isothiocyanates combine with phosphonohydrazidic and phosphonohydrazidothioic acid; methyl isothiocyanate does not react with these hydrazides.

Chlorophenyl isocyanate and phenyl isothiocyanate add to methyl phosphorodihydrazidothioate with formation of bis-(semicarbazido)- and bis(thiosemicarbazido)-methylphosphonothioates.[69] The β-structure of the compounds obtained has been demonstrated by IR and $^1$H NMR spectroscopy.[69,89]

Analysis of a series of studies on the mechanisms and kinetics of the reactions of phosphorus acid hydrazides with isocyanates and isothiocyanates[90–94] permits the following conclusions.

Since the reactions of diarylphosphinic hydrazides and diaryl phosphorohydrazidates with phenyl isocyanate[90] are nucleophilic addition reactions, it follows that, by analogy with the reactions of carboxylic acid hydrazides with isocyanates,[95,96] one can postulate that they proceed via a multistage addition mechanism with formation of a tetrahedral intermediate:




The decomposition of the intermediate is facilitated by the formation of a hydrogen bond between the hydrogen atom of the imino-group of the hydrazide and the electronegative oxygen or nitrogen atom of the isocyanate. The substitution of the hydrogen atom of the imino-group by the ethyl group rules out the formation of an intramolecular hydrogen bond, which decreases the rate constants for the reactions of diarylphosphinic 1-ethylhydrazides and phosphoro(1-ethylhydrazidates) with isocyanates.

The kinetics of the reactions of diarylphosphinic hydrazides and diaryl phosphorohydrazidates,[90] diaryl phosphorohydrazidothioates,[91] and diaryl phosphoro(1-ethylhydrazido)-thioates[92] with phenyl isocyanate in benzene have been investigated at different temperatures. The rate constants calculated from a second-order equation remain satisfactorily invariant during the process at different concentrations of the initial reactants in the presence of the reaction products.

The reactions of phosphorus acid hydrazide with phenyl isocyanate proceed with low activation energies and high negative activation entropies. The high negative activation entropies ($\Delta S^{\neq} = -49.5$–$57.4$) in the above reactions show that the approach of the electrophile to the molecule of a hydrazide having a tetrahedral configuration is sterically more hindered than the approach to the planar molecule of a carbonyl-containing hydrazide ($\Delta S^{\neq}$ for the reaction of benzoyl hydrazide with phenyl isocyanate is −41.8 cal mol$^{-1}$ K$^{-1}$).[95] The reactivities of the phosphorus acid hydrazides investigated vary in parallel with the basicity constants of the hydrazides.

The kinetics of the reactions of phosphorus acid hydrazides and 1-ethyl hydrazides with phenyl isothiocyanate in benzene have also been investigated. The reaction takes place quantitatively with formation of phosphorus acid thiosemicarbazides. The kinetics of these reactions are described by a second-order equation and the rate constants calculated from these equations remain satisfactorily invariant throughout the process.[93]

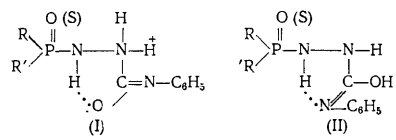
In the study of the kinetics of the reactions of phosphorus acid hydrazides with phenyl isocyanate,[97] questions concerning the influence of solvents on the rate and mechanism of this reaction were considered. The catalytic activity of dimethylformamide, dioxan, and pyridine in the reactions of diphenylphosphinic acid [hydrazide?] with phenyl isocyanate and picryl chloride shows that the solvation of the initial or transition state, involving the more acidic hydrogen atom of the imino-group in the initial hydrazide, is of decisive importance.

*(i) The α-Effect in Reactions with Electrophiles*

The α-effect is manifested as a positive deviation of the point corresponding to α-nucleophiles from the Brønsted straight line for compounds with the usual reactivity. Quantitatively the α-effect is defined as the ratio of the rate constants in the reactions of the α-nucleophile and a primary aromatic amine of equal basicity.

Hydrazine and its derivatives exhibit an enhanced reactivity in reactions with carbonyl- and sulphonyl-containing compounds.[94,98] Under the influence of the substituents in the aromatic rings of phosphorus acid hydrazides, the α-effect in the reaction changes.[8,90–94] However, the sequence in which the α-effect varies under the influence of such substituents is different in different series. In the reactions of diarylphosphinic hydrazides with phenyl isocyanate and picryl chloride,[8,90] electron-donating substituents reduce the α-effect, while electron-donating accepting substituents increase it. On the other hand, in the reactions of diaryl phosphorohydrazidates, diaryl phosphorohydrazidothioates,[90,92] and diaryl phosphoro(1-ethylhydrazido)thioates[94] with phenyl isocyanate, the substituents in the aromatic ring exert the opposite influence. The α-effect is linearly related to the basicity constants of the hydrazides.

Several possible causes of the manifestation of the α-effect have now been established but none, considered separately, can fully account for the nature of the phenomenon under consideration. On the assumption that the α-effect is to a large extent determined by the structure of the transition state, the enhanced reactivity of phosphorus acid hydrazides can be explained by their ability to form the cyclic complex (I) and (II) via a hydrogen bond between the oxygen or nitrogen atom of phenyl isocyanate and the hydrogen atom of the imino-group and also via a new bond between the carbon atom and the amino-group of the nucleophile.



(I) (II)

The transition states are distinguished by high stability as a consequence of the aromatic character and the presence of $4n + 2$ electrons. In addition a cyclic transition state promotes a more complete shift of the electron pair from the nucleophilic centre, facilitating thereby the formation of a new C–N bond.

In the reactions of phosphorus acid hydrazides with phenyl isothiocyanate, an appreciable decrease of the α-effect is observed compared with phenyl isocyanate, which can be explained by the lower capacity of the sulphur atom for the formation of a hydrogen bond in the transition state, which reduces the possibility of the formation of the cyclic complexes (I) and (II).[99]

Thus the extent to which the α-effect is manifested depends on the nature of both the nucleophile and the substrate and depends on the reaction mechanism. The reactions of phosphorus acid hydrazides involving the formation of cyclic atomatic complexes are energetically more favourable and are characterised by a higher α-effect.

## 2. Reactions with Nucleophiles

### *(a) Interaction with Ethanol and Diaryl Phosphoric acids*

In order to discover the possible phosphorylating properties of phosphorodi(*NN*-alkylarylamidic) hydrazides, a study was made of their interaction with various nucleophiles in the presence of iodine:[79] ethanol, diphenyl phosphoric acid, and phosphorodi(*N*-phenylamidic) acid. The synthesis was carried out in accordance with the following scheme:

$$(C_6H_5NR)_2\overset{O}{\overset{\|}{P}}NHNH_2 + HX \xrightarrow{I_2} (C_6H_5NR)_2\overset{O}{\overset{\|}{P}}X +$$

$$+ (C_6H_5NR)_2\overset{O}{\overset{\|}{P}}OP(O)(NHC_6H_5)(RNC_6H_5) + (C_6H_5NR)_2\overset{O}{\overset{\|}{P}}OP(O)(RNC_6H_5)_2 ;$$

R=CH$_3$, X=OC$_2$H$_5$; R=CH$_3$, X=OP(O)(OC$_6$H$_5$)$_2$;

R=CH$_3$, X=OP(O)(NHC$_6$H$_5$)$_2$ .

Phosphorodi(*NN*-cyclohexylphenylamidic)hydrazides are phosphorylating agents and give rise to the corresponding pyrophosphates on reaction with phosphorodi(*N*-arylamidic) acids:[79]

$$(RNH_2)_2\overset{O}{\overset{\|}{P}}NHNH_2 + (R'NH)_2\overset{O}{\overset{\|}{P}}OH \xrightarrow{I_2} (RNH)_2\overset{O}{\overset{\|}{P}}OP(O)(NHR')_2 .$$

### *(b) Interaction with Water, Caustic Alkalies, Hydrogen Chloride, and Nitric Acid*

It is known that in the presence of moisture one ester linkage in diaryl phosphorohydrazides is hydrolysed:[16]

$$(C_6H_5O)_2\overset{O}{\overset{\|}{P}}NHNH_2 + H_2O \rightarrow H[PO_2(OC_6H_5)(NHNH_2)] + C_6H_5OH .$$

Diaryl phosphorohydrazidates are stable only in the absolutely dry state.

In the reactions of diaryl phosphorohydrazidates and *OO'*-diaryl phosphorohydrazidothioates with caustic alkalies, the hydrolysis of one or two ester linkages, depending on reaction conditions, is observed, with formation of the mono- and di-sodium (potassium) salts of phosphorus acid hydrazides. The ester linkage is also hydrolysed in the hydrolysis of phenyl phosphorodihydrazidate and *O*-phenyl phosphorodihydrazidothioate[16,42] with formation of a salt. When sodium (potassium) salts of phosphorus acid hydrazides are treated with hydrochloric and acetic acids, the corresponding acids are produced.[16]

*N*-Substituted phosphorus acid hydrazides react with hydrochloric acid to form several products:[100]

$$(CH_3)_3C\overset{O}{\overset{\|}{P}}(OCH_3)NC(CH_3)_3NHC(CH_3)_3 \xrightarrow[15\ min]{6M\,HCl} (CH_3)_3C\overset{O}{\overset{\|}{P}}(OCH_3)NHNHC(CH_3)_3 \xrightarrow{\Delta}$$

$$\rightarrow (CH_3)_3C\overset{O}{\overset{\|}{P}}(OH)_2 + (CH_3)_3CNHNHC(CH_3)_3 \cdot HCl + (CH_3)_3CNHNH_2 \cdot HCl .$$

*t*-Butylhydrazine hydrochloride is formed from 1,2-di-t-butylhydrazine as a result of the dissociation of the C–N bond. On further hydrolysis, trimethylmethanol, chloromethane, and methanol were isolated.

On interaction with dry hydrogen chloride, phosphorus acid hydrazides form hydrochloride salts of the following type:[25,34,101]

$$(C_2H_5O)(o\text{-}ClC_6H_4O)\overset{X}{\overset{\|}{P}}NHNH_2 \cdot HCl ;$$

$$(ClCH_2CH_2)_2\overset{O}{\overset{\|}{P}}(OAr)NHNH_2 \cdot HCl ;$$

X=O; S .

On treatment with sodium nitrite in solution in hydrochloric acid, phosphorodi[*N*-cyclohexyl(benzyl)amidic] hydrazides are converted into phosphorodi(*N*-cyclohexylamidic) and phosphorodi(*N*-benzylamidic) azides.[24] The structure of the azides has been demonstrated by IR spectroscopy: $\nu_{max}$(NH) = 3368, 3260, and 3220 cm$^{-1}$; $\nu(N_3)$ = 2150–2140 cm$^{-1}$; $\nu$(P=O) = 1210–1205 cm$^{-1}$.

### 3. Oxidation Reactions

The oxidation of phosphorodi(*NN*-alkylarylamidic) 2-methoxy(ethoxy)carbonylhydrazides with lead tetra-acetate leads to the formation of the corresponding azo-derivatives:[79]

$$(C_6H_5NR)_2\overset{\overset{O}{\|}}{P}NHNHR' + Pb(OAc)_4 \rightarrow (C_6H_5NR)_2\overset{\overset{O}{\|}}{P}N{=}NR + Pb(OAc)_2 + AcOH\ ;$$
$$R{=}CH_3,\ C_2H_5;\ R'{=}COOC_2H_5,\ C_6H_5\ .$$

The relation is carried out in a 20 : 1 mixture of absolute chloroform and glacial acetic acid at 0 °C. Phosphorodi(*NN*-methylphenylamidic) 2-toluene-*p*-sulphonylhydrazide decomposes vigorously under the conditions of this reaction.

Bromosuccinimide, mercury(II) oxide, and nitrogen dioxide are weak oxidants. The oxidation with bromosuccinimide is carried out in absolute chloroform at −5 °C in accordance with the following scheme:

$$(C_6H_5O)_2\overset{\overset{O}{\|}}{P}NHNHCOOC_2H_5 + \begin{matrix}CH_2{-}CO\\ \\ CH_2{-}CO\end{matrix}\!\!>\!NBr \rightarrow (C_6H_5O)_2\overset{\overset{O}{\|}}{P}N{=}NCOOC_2H_5\ .$$

*N*-Unsubstituted hydrazides of phosphorus diesters are oxidised by iodine in aqueous solutions in the presence of tertiary amines with liberation of nitrogen and the formation of phosphoric acid diesters.[102]

### 4. Acid–Base Properties

The presence of nitrogen atoms together with the nucleophilic phosphorus atom results in the manifestation of amphoteric properties by phosphorus acid hydrazides. In connection with the investigation of the acid–base properties of phosphorus acid hydrazides, studies were made of the basic ($pK_{a_1}$) and acid ($pK_{a_2}$) ionisation constants of diarylphosphinic hydrazides and diarylphosphorohydrazidates[90,93] and the basic ionisation constants ($pK_{a_1}$) of *OO'*-diaryl phosphorothioates and *OO'*-diaryl phosphoro(1-ethylhydrazido)thioates have been determined.[91,92] Analysis of the data obtained showed that the ionisation constants of phosphorus acid hydrazides are satisfactorily correlated with $\Sigma\sigma^{ph}$;

$$pK_{a_1} = 2.57-0.37\sum\sigma^{ph}\ (r = 0.992;\ S = 0.0222)\ \ [90]$$
$$pK_{a_2} = 12.78-0.54\sum\sigma^{ph}\ (r = 0.99,\ S = 0.006)\ .$$

Comparison of the constants ρ in the equation shows that the secondary amino-group is more sensitive to structural changes in the diphenylphosphinic hydrazide molecule than the primary amino-group, which is more remote from the substituents. The same behaviour has been observed for the hydrazides of aromatic carboxylic acids.[103,104]

The acid–base properties of the hydrochlorides of aryl phosphoro[*NN*-di(2-chloroethyl)amido]hydrazidates, whose ionisation constants are satisfactorily linearly related to the Hammett $\sigma^0$ constants and Taft $\sigma^*$ constants, have been investigated:[105]

$$pK_a = 3.20-1.04\sigma^0\ \rho = -1.04\ (r = 0.99;\ S = 0.028)\ .$$

The constant ρ = −1.04 for aryl phosphoro[*NN*-di(2-chloroethyl)amido]hydrazidates compared with ρ = −0.37 for diarylphosphinic hydrazides indicates a greater sensitivity of phosphorohydrazidates to structural changes than that of the phosphinic acid derivatives.

### 5. Polarography of Phosphorus Acid Hydrazides

The polarographic behaviour of aryl phosphoro[*NN*-di(2-chloroethyl)amido]hydrazidates has been investigated.[105] The study of the half-wave potentials of phosphorus acid hydrazides containing the di(2-chloroethyl)amino-group showed that these quantities are in the range from −1.30 to −1.45 V. Satisfactory results have been obtained in alkaline media at pH 9.2, in agreement with literature data for the polarographic activity of the chloroethylamino-group.[106] The influence of various substituents in the *para*-position in the aromatic ring on the polarographic reduction has been estimated. The constant $\rho^* = 0.23$ ($r = 0.99$; $S = \pm 0.025$). The positive value of $\rho^*$ shows that the primary reaction at the electrode involves nucleophilic attack on the electron of the bond being reduced and the comparatively low value of $\rho^*$ indicates a weak influence of the substituents on the electrochemical reaction.

The replacement of the hydrogen atom in the hydrazide group by the toluene-*p*-sulphonyl group changes the direction of the oxidation-reduction process, the sign of the constant $\rho^*$ for which alternates.[63]

### 6. Spectroscopic Properties

The most varied physicochemical methods have been used to study the structure of phosphorus acid hydrazides: IR, UV, and $^1H$ NMR spectroscopy;[24,34,48,56,69,70,73,75,89] the present Section deals with problems in the IR spectroscopic study of the influence of electron-donating and electron-accepting substituents in the aromatic ring on the shift of the bands due to the NH and P=O groups.[90–92]

The complex behaviour of the spectroscopic characteristics of the stretching vibrations of the NH groups in phosphorus acid hydrazides is due to the presence of the imino- and amino-groups at different distances from the P=O group in the aromatic ring and interacting with one another. The influence of substituents on the stretching vibrations of the imino-group (NH) is dominant and is transmitted more effectively by virtue of the considerable amount of double bond character of the P–N bond. The influence of the substituent on the amino-group is transmitted via more extensive molecular systems, incorporating the N–N unit, where the transmission of the electronic influence takes place solely via the *I* effect.

Studies of the IR spectra of diaryl phosphorohydrazidates and *OO'*-diaryl phosphorohydrazidothioates and of the influence of electron-donating and electron-accepting substituents in the aromatic ring on the NH and P=O band shift have been reported.[90–92]

The IR absorption spectra of diaryl phosphorohydrazidates show the following frequencues: ν(P=O) = 1191–1213 $cm^{-1}$, ν(NH) = 3368–3321 and 3227–3204 $cm^{-1}$; the frequencies in the spectra of *OO'*-diaryl phosphorohydrazidothioates are as follows: ν(P=S) = 660–652 $cm^{-1}$ and ν(NH) = 3350–3330 and 3195–3138 $cm^{-1}$.

The NH and P=O stretching vibration frequencies of diaryl phosphorohydrazidates are satisfactorily correlated with the constants $\sigma^{ph}$ and can be expressed by the following equations:

$$\nu(NH) = 3222+45\sum\sigma^{ph}\ (r = 0.868;\ S \pm 4.889)\ ;$$
$$\nu(NH') = 3327-63\sum\sigma^{ph}\ (r = 0.945;\ S \pm 3.958)\ ;$$
$$\nu(P{=}O) = 1206+51\sum\sigma^{ph}\ (r = 0.987;\ S \pm 1.526)\ .$$

The stretching vibration frequencies in *OO'*-diaryl phosphorohydrazidothioates change slightly under the influence

of substituents of different electronic nature. A tendency is observed towards a linear relation between the logarithms of the reaction rate constants and the NH and P=S stretching vibration frequencies.

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# Computer Modelling of Dense Polymer Systems

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The application of the Monte Carlo method and the methods of molecular and Brownian dynamics to the study of the structures and dynamic properties of dense polymer systems with a strong intermolecular interaction is examined. The methodological problems arising in the computer modelling of polymers are discussed. Data obtained in numerical experiments on computers for solutions of macromolecules in a low-molecular-weight solvent, semidilute polymer solutions, liquid and amorphous polymers, as well as partly ordered systems (liquid and rotation crystals) are surveyed. The results of the computer experiments are compared with the conclusions arising from modern analytical theory. The limitations of the numerical methods and the prospects for their further development are considered.
The bibliography includes 195 references.

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## I. INTRODUCTION

In connection with the progress in computer technology, methods involving the computer simulation of the mathematical models of various physical systems have come to be widely used in recent years. Such models include primarily those of many non-ordered systems with a strong interaction between species: molecular liquids, liquid metals, dense gases and plasma, polymer solutions and melts, liquid crystals, etc.

Three principal computer simulations methods are used in the solution of a whole series of problems in the physics and chemistry of polymers: the Monte Carlo method (MC) and the methods of molecular dynamics (MD) and Brownian dynamics (BD). In the MC method the required properties are obtained by averaging over an *ensemble* of configurations of the system generated on a computer with the aid of a suitable algorithm. The most detailed information (both equilibrium and dynamic) is provided by the MD method, which consists of the numerical integration of the equations of motion formulated in classical mechanics for all the particles of the system under specified initial conditions. The BD method yields a more detailed picture; in this method the influence of the medium (solvent) is taken into account as the overall effect of the forces of viscous friction and random forces.

In the vast majority of studies on the computer modelling of polymers (starting with that of Wall et al.),[1] the influence of volume (long-range) interactions on the conformation of an isolated macromolecule has been investigated by the MC method. The real macromolecule is usually represented in such calculations by a broken line executing random movements on a regular lattice of a specified type (cubic, tetrahedral, etc.). The surrounding solvent is not then taken into account explicitly on the assumption that its role reduces wholly to an effective renormalisation of the interaction potentials of the units of the macromolecule. There exist reviews of early studies in this field.[2-4]

The increase of the power of computers made it possible to formulate computer experiments with more complex models. On the one hand, it became possible to specify in greater detail the models of macromolecules themselves, including the calculations of data concerning chemical structure, inhibiting potentials, etc. Studies have been made on the modelling of a whole series of synthetic polymers,[5-9] polypeptides,[10] polynucleotides,[11] and polysaccharides (for example amylose[12] and cellulose derivatives).[13] On the other hand, the MC and MD methods have come to be used in the study of condensed polymer systems with direct allowance for the influence of the molecules of the medium and of the interaction between molecules. Such investigations are analysed in this review.

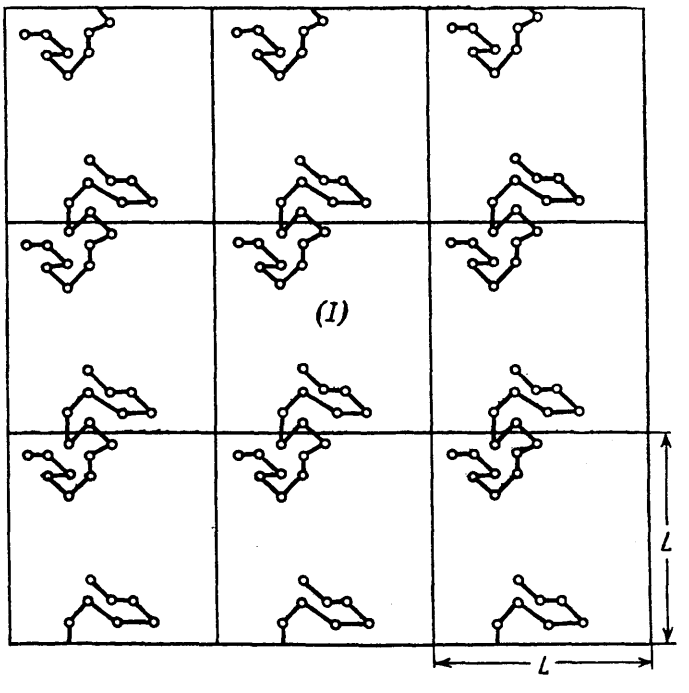



Figure 1. Planar projection of the computational cell (I) with periodic conditions on the boundaries. The cell contains one chain; the solvent particles are not shown.

## II. DILUTE SOLUTIONS

### 1. Methodological Problems

In the computer modelling of dilute polymer solutions (macromolecule + dense low-molecular-weight liquid) all the particles (species) are placed in a cell which usually has the form of a cube with a specified edge $L$ (Fig.1). In order to eliminate surface effects, periodic boundary conditions are introduced: the main cell is surrounded on all sides by similar cells. Free exchange of particles between the cells through the walls is possible. In addition, in dynamic methods a particle which enters the main cell from a neighbouring cell has the same momentum as the particle crossing the wall. We may note that the periodic conditions can be introduced in a different way by placing the molecules not in a cube but on the surface of a hypersphere with a specified radius and number of dimensions exceeding by unity that of the system being modelled.[14]

It is noteworthy that, among polymer systems, dilute solutions are the most inconvenient objects for computer modelling. The point is that, although the polymer molecule is of principal interest, nevertheless most computational effort is expended not on its investigation but on following the movement of solvent molecules, because the number of the latter in the cell is usually much greater than the number of polymer units. Indeed, in order to eliminate the interaction of the chains, it is necessary that the length of the edge of the cell should exceed the maximum size of the macromolecular chain. Consequently, in modelling even an extremely short chain, for example, one made up of 20 units with a contour having a length of ~20, the computational cell must contain ~$10^4$ solvent species when the density of the liquid, $\rho \cong 1$. Such systems lie at the limit of the capacity of the majority of modern computers. Furthermore, as in a physical experiment, the smallness of the observed effects is characteristic of the study of dilute solutions by computer methods. Before proceeding to the discussion of specific results, it is necessary to deal with certain new procedures for increasing the effectiveness of the calculations and also to examine the specific features which arise in the mathematical modelling of polymer systems.

We shall consider a system of $N$ interacting particles with a specified pair potential $f(r_{ij})$, where $\mathbf{r} = (\mathbf{r}_1,...,\mathbf{r}_N)$ are the radius-vectors of the particles which determine the configuration of the system and its potential energy:

$$U(\mathbf{r}) = \frac{1}{2}\sum_i^N \sum_j^N f(r_{ij}).$$

In the classical Metropolis scheme[15,16] the transitions between the configurations take place as follows. After a random selection of a particle $i$ and its displacement in a random direction ($\mathbf{r}_i \to \mathbf{r}_i'$) over a distance $\leq\delta$, the transition to the new configuration ($\mathbf{r} \to \mathbf{r}'$) takes place with the probablilty

$$p = \min\{1, q(\mathbf{r}, \mathbf{r}')\}, \qquad (1)$$

where $q(\mathbf{r},\mathbf{r}') = \exp[(U - U')/kT]$, $U$ and $U'$ being the corresponding potential energies. The system remains in the old state $\mathbf{r}$ with the probability $1 - p$. The formulation (1) means that $p$ is equal to the smallest of the numbers in braces. The random selection process and the subsequent attempt to shift the particle (step) are repeated in the MC method a large number of times, $s$ (~$10^3$–$10^5$ steps per particle); the required characteristic is averaged over all the $s$ steps. The resulting estimate at $s \to \infty$ tends to the true mean over the canonical *ensemble*.

In order to accelerate the convergence of the computational procedure, it has been suggested[17,18] that the Metropolis scheme be modified in such a way that the selected particle moves with a higher probability in the direction of the instantaneous force acting on it from the sides of all the remaining particles. In this algorithm, called the "force bias method", the new configuration is achieved with a probability

$$p = \min\left\{1, q(\mathbf{r}, \mathbf{r}') \cdot \frac{T(\mathbf{r}', \mathbf{r})}{T(\mathbf{r}, \mathbf{r}')}\right\} \qquad (2)$$

where $q$ is specified by Eqn.(1) and the quantity $T(\mathbf{r}, \mathbf{r}')$, linked to the transition $\mathbf{r} \to \mathbf{r}'$, is determined from the formula

$$T(\mathbf{r}, \mathbf{r}') = \begin{cases} C \cdot \exp(\lambda \Delta\mathbf{r} \cdot \mathbf{F}_i/kT) & \text{when } \Delta r \leqslant \delta \\ 0 & \text{when } \Delta r > \delta \end{cases} \qquad (3)$$

For the reverse transition, the quantity $T(\mathbf{r}', \mathbf{r})$ has an analogous form. In Eqn.(3), $\Delta\mathbf{r} = \mathbf{r}_i' - \mathbf{r}_i$ is the shift of the $i$th particle within the limits of the specified region $\delta$, $\mathbf{F}_i = -\partial U(\mathbf{r})/\partial \mathbf{r}_i$ the force acting on the particle in the configuration $\mathbf{r}$, $\lambda$ a parameter, and $C$ the normalising constant, which cancels out in Eqn.(2). It is seen from Eqns. (2) and (3) that the particles are displaced predominantly in the direction of the force $\mathbf{F}$. For $\lambda = 0$, the scheme described reduces to the Metropolis scheme. The parameters $\lambda$ and $\delta$ are chosen in such a way that the mean square shift of the particles is maximised.

A MC algorithm, formally similar to the method of Brownian dynamics, has been proposed[19–21] and Rossky et al.[19] called it SMART. If an $N$-unit chain is immersed in a viscous medium, then the movement of any $i$th particle (unit) can be described by the Langevin equation[22]

$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = -m_i\gamma_i \frac{d\mathbf{r}_i}{dt} + \mathbf{F}_i + \mathbf{R}_i, \quad i = 1, 2, \ldots, N, \qquad (4)$$

where $m_i$ and $\gamma_i$ are respectively the mass and the coefficient of friction, $\mathbf{F}_i$ is the force acting on the $i$th particle from the side of all the remaining particles of the chain, and $\mathbf{R}_i$ is a random force reflecting the random jolts by other molecules of the medium. In a real situation, Eqn.(4) should include the hydrodynamic forces, but one can consider a highly viscous medium ($\gamma \gg 1$) where they are absent. In this case the inertial term on the left-hand side of Eqn.(4) can also be rejected. The following algorithm of motion, formulated in the finite difference form

$$\mathbf{r}_i' = \mathbf{r}_i + \Delta t D_i \mathbf{F}_i/kT + \mathbf{X}_i, \quad i = 1, 2, \ldots, N, \qquad (5)$$

is then obtained. Here $|\mathbf{r}_i' - \mathbf{r}_i|$ is the distance traversed by the $i$th particle during the period $\Delta t$, $D_i = kT/m_i\gamma_i$ the diffusion coefficient of the particle, and $\mathbf{X}_i$ the random shift corresponding to the force $\mathbf{R}_i$ and having the normalised Gaussian distribution

$$W(X_{i\alpha}) = (4\pi a_i)^{-1/2} \cdot \exp(-X_{i\alpha}^2/4a_i), \quad \alpha = x, y, z, \qquad (6)$$

where $a_i = \Delta t D_i$ is the specified parameter.

In Brownian dynamics the equation of motion (5) describes a sequence of unconditional transitions between states. In the MC method the new position $\mathbf{r}'$ in Eqn.(5) is adopted or rejected with a probability defined by Eqn.(2), where

$$T(\mathbf{r}, \mathbf{r}') = (4\pi a_i)^{-3/2} \cdot \exp\{-[(\mathbf{r}_i' - \mathbf{r}_i) - a_i \mathbf{F}_i/kT]^2/4a_i\}, \qquad (7)$$

and $T(\mathbf{r}', \mathbf{r})$ is formulated analogously. Compared with the standard scheme,[15] the "force bias" and SMART algorithms ensure an increase of the probability of the transition defined by Eqn.(1) by a factor of ~2–3.

Finally mention should be made of a fundamentally new approach to the MC modelling of chains based on the functional integration technique. In contrast to the usual treatment of the "chain–set of discrete force centres (units)" system, it has been suggested[23] that the macromolecule be described by a continuous line specified by a Fourier series in functional space. For a random selection of the series coefficients, the line changes its shape (i.e. it undergoes "conformational rearrangements") and the transitions between states evolve in accordance with the usual MC scheme.

In the study of polymers by the MD method, the problem of the way in which the valence bonds are described becomes important. Here there are alternatives: (1) the bonds can be modelled by any smooth function (for example, a quadratic function) and (2) the bonds can be regarded as absolutely rigid bounded formations, i.e. they are modelled by a $\delta$-function. In the former case the standard difference schemes of computational mathematics are suitable for the integration of the equations of motion $m_i d^2\mathbf{r}_i/dt^2 = \mathbf{F}_i$,[24] which make it possible to find the coordinates and momenta of the particles at finite time intervals $\Delta t$. However, owing to the great "rigidity" of the valence potentials, high-frequency oscillations are characteristic of the chain particles which can be taken into account only for a very small integration step $\Delta t$. This shortens the length of the trajectory susceptible to calculations. For this reason, the exclusion from the calculation of the corresponding degrees of freedom when chemical bonds are treated as geometrical bounded regions gives rise to a considerable computational effect.

Within the framework of this method of modelling, special procedures, correcting the bond length at each step, are used. One of the correction procedures has been proposed by Balabaev[25] and another, the widely used procedure SHAKE, has been put forward by Ryckaert et al.[26] An improved version of the algorithm SHAKE, which the author called RATTLE, has been proposed.[27] The specific features of the mathematical modelling of polymers by the MD method consist precisely in the presence of such correction procedures. Without any changes, they also enter into the BD method, which is based on the numerical integration of the Langevin equation. The algorithms used at present for calculations by the BD method (including those taking into account hydrodynamic interactions[29] and the random force delay effects)[30] have been published.[28–30] Both dynamic methods yield a phase trajectory from which the equilibrium characteristics (as time averages) and the time variations are determined.

In conclusion of this Section, we shall make two general remarks: about the relation between the computer methods and about their correspondence to a real experiment. As already stated, the physical principles on which the MC and MD modelling is based differ radically. In the former case these are the probability principles of statistical mechanics and in the latter they are the extremely deterministic foundations of classical Newtonian mechanics. The BD method, in which stochastic and determined descriptions are combined, occupies an intermediate position in this sense.

The question of the equivalence of the equilibrium properties obtained by averaging with respect to the *ensemble* and time along the dynamic trajectory is actually identical with the familiar ergodic problem. If there exists a thermodynamic limit $(N, V)_{N, V \to \infty} = \text{const}$. (where $V$ is the volume), then there is no doubt about the validity of the different types of averaging. Systems made up of a finite number $N$ of particles require a more careful analysis. We may note that such a problem can be solved within the framework of the computer calculations themselves. It is found that the results of the averaging by both methods differ by a quantity of the order of $1/N$.

Another part of the problem of the relation between the computer methods reduces to the dynamic interpretation of the Monte Carlo process. This treatment is based on the fact that the Metropolis scheme (or its modifications) reproduces the evolution process in which the system passes step by step from one state to another and the consecutive states are highly correlated. Naturally, such evolution self-models a kind of artificial (stochastic) kinetics, but it does not reflect the real alternation of the states of the system in real time, as happens in molecular dynamics. Nevertheless, it is possible to define conditions for which the MC method yields the correct description of the kinetic behaviour. It has been recently demonstrated rigorously[31] that, within the limits of a small step ($\delta \to 0$), in the usual MC calculation the configuration relaxation is described by the same kinetic relations as in the modelling by the BD method at the limit corresponding to a high friction, where $\gamma \gg 1$ and the non-inertial movement of the particles follows the Langevin equation (5). The Monte Carlo time scale (i.e. the number of steps per particle) and the real time $t$ are then linearly related: $s/N \cong Tt/\gamma\delta^2$, which is valid in practice for a fairly large step $\delta$. Therefore, having followed by the two methods the evolution of any one function of the coordinates, it is possible to correlate the time scales and thereby establish a relation between the results of the statistical and dynamic modelling.

Thus the computer simulation methods, based on different physical principles, have a most important advantage—they are closed, i.e. there is a possibility of a mutual test within the very results obtained for the same model.

The principal problems in the computer experiment arise in connection with the formulation of the model of the test object. This concept includes primarily the set of rules describing the interaction of the particles with one another or with external fields. The way in which the valence forces, i.e. the chemical combination of atoms, are taken into account is one of the examples of such rules. Since different kinds of valence and non-valence potentials, which constitute merely an approximation to the true interaction, are used for this purpose, this in fact defines a measure of the correspondence between the physical and computer experiments. Naturally, initially it is possible to solve the converse problem, where the potentials are at first calibrated against the available experimental data and are only then used to obtain more detailed information about the system. On the other hand, since numerical experiments for the specified model yield rigorous results within the limits of statistical error, they can be adopted as a standard to test the theories relevant to an analogous model and the approximations on which the analytical treatment is based. We believe that this precise formulation of the problem is methodologically justified. However, in both cases one must remember (and this is the principal limitation) that any modern computer can operate only with an immeasurably smaller number of particles than in real systems, where $N \cong 10^{23}$. The "record" calculations, familiar to the authors, on the most powerful multiprocessor or vector computers (of the PS-3000 or CRAY type) are restricted to models comprising $N \cong 10^6$ particles and times $t \sim 10^{-6}$ s†, which are very small on the macroscopic scale. As a rule, calculations are in fact performed for $N \cong 10^2$–$10^3$ and a time interval $T \lesssim 10^{-9}$ s.

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†The symbol ~ is used in Russian to imply "proportional to", "of the order of", or even "approximately equal". No attempt has been made in the translation to elucidate its specific meaning in each use (Ed. of Translation).

Although small systems, such as molecular clusters or isolated macromolecules, are of independent interest, in the usual practice employed in computer calculations the interpretation of macroscopic properties on the basis of the modelling of a set of a small number of particles is an extremely non-trivial problem. The greatest difficulties are associated with the study of systems near phase transition points where large-scale low-frequency fluctuations arise. An extensive literature[16,24] has been devoted to the analysis of such problems, which we are unable to consider in detail here. We shall only note that, when periodic boundary conditions are used for the extrapolation to the thermodynamic limit, it is essential that the linear size of the cell $L(L \sim N^{1/d}$ in a $d$-dimensional space) should exceed significantly the correlation radius of the density fluctuations. If the calculation is not performed near a phase transition point, then for the usual short-range potentials this requirement is normally satisfied for $N \sim 10^2-10^3$ and the error due to the finite size is of the order of $1/N \sim 1/L^d$.

## 2. Equilibrium Properties

Since macromolecular compounds cannot be transferred to the gas phase, the question of the influence of the solvent on their conformation and movement is fundamental. It is important also from the methodological point of view. In fact the justification of the computer experiments in which the solvent is not considered explicitly and is taken into account either via the potential of the average force of interaction of the units or as a continuous viscous medium generating random jolts actually depends on the solution of this kind of problem.

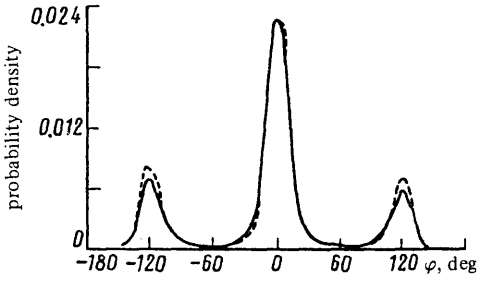



**Figure 2.** Distribution function with respect to torsional angles $\phi$ of the central C–C bond for n-butane at 218 K.[32] Continuous line—gas; dashed line—solution in $CCL_4$; the angle $\phi = 0$ corresponds to the *trans*-conformation.

A system comprising one n-butane molecule and 127 carbon tetrachloride molecules with an overall density of 1.61 g cm$^{-3}$ has been investigated by the MC method.[32] The interaction of the particles was described by the Lennard-Jones potential and the hindrance to the internal rotations around its central C–C bond in butane was described by a three-barrier cosinusoidal potential $V(\phi)$. The transitions between the configurations evolved in conformity with the Metropolis scheme.[15] Analysis of the distribution with respect to the angles of internal rotation showed (Fig. 2) that these distributions are virtually identical for both dissolved and isolated (present in a rarefied gas) butane molecules. In both cases the most probable values of $\phi$ are 0° and ±120°. The fractions of the *trans*-isomers also proved to be similar: 0.61 and 0.65. Consequently one may say that, within the limits of the accuracy of the calculation, the solvent does not exert an appreciable influence on the conformation of n-butane. Robertus et al.,[33] who modelled a dilute solution of n-butane by the MD method, arrived at the same conclusion.

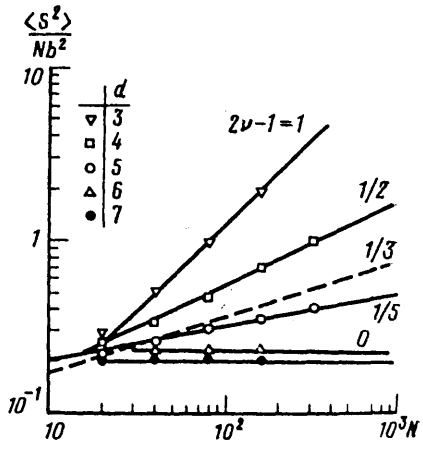



**Figure 3.** Dependence of the mean square radius of inertia of a charged chain on the number of units for spaces with different numbers of dimensions $d$.[47] Symbols—MC calculations; continuous lines—calculation based on the Flory theory; dashed line—calculation by the RG method for $d = 5$.

Naturally the calculations for n-butane do not reflect quite adequately the properties of long chains. Computer experiments on the modelling of chains with a large number of units are therefore of special interest. We may note the studies [34–41] in which the MD method has been used. In the first investigations of this kind[34,39] a nine-unit chain ($N = 9$), placed in a cell which also contained $N_S = 855$ solvent molecules, was studied. The interaction between any two particles in the system was described by the Lennard-Jones potential

$$f(r_{ij}) = 4\varepsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}], \qquad (8)$$

where $r_{ij}$ is the distance between the particles $i$ and $j$ and $\varepsilon$ and $\sigma$ are parameters. We may recall that reduced units are employed in the MD method: the lengths are expressed in units of $\sigma$, the rates in units of $(\varepsilon/m)^{1/2}$, and the time in units of $\tau = \sigma(m/\varepsilon)^{1/2}$, where $m$ is the mass (the mass was assumed to be the same for all the particles[34,39]). The chain considered in the above studies[34,39] contained bonds with a rigorously fixed length but the angles between the bonds and the angles of internal rotation were not restricted. The number-average density of the system was $\rho = (N + N_S)L^3 = 0.85$. As a result of averaging with respect to a trajectory whose length was 142$\tau$, the mean square of the distance between the ends of the chain $\langle R^2\rangle$ and the mean square radius of inertia $\langle S^2\rangle$ were found. In addition, the static structure factor $s(Q)$ was calculated for $|Q| \leq 40/\sigma$. For comparison, all the calculations were repeated for the same chain but without taking into account the solvent. It was found that in both cases the average

dimensions of the chains are similar. The functions $s(Q)$ are also virtually identical. Small differences were observed in the region of small $Q \leqslant 1.5/\sigma$ corresponding to units remote from one another. The characteristics of the average form of the polymer coil (i.e. the relations between the orthogonal components of the radius of inertia) also do not exhibit appreciable differences.

Rapaport,[36] who investigated by the MD method freely jointed chains comprising 5, 10, and 20 units immersed in a solvent with $\rho = 0.2$ or 0.3, arrived at analogous conclusions. It was shown that the quantities $\langle R^2 \rangle$ and $\langle S^2 \rangle$ agree satisfactorily with the results of a previous calculation,[42] where the solvent was altogether disregarded.

We may also note a study[41] of the MD modelling of a dense system ($\rho = 0.85$) comprising 246 solvent particles and one ten unit chain with fixed skeletal angles and bonds and with hindered rotation. Calculations taking into account the strong attraction between all the system particles showed that the quantities $\langle R^2 \rangle$ and $\langle S^2 \rangle$ are somewhat greater than in the case of a purely repulsive potential. In our view, this effect is due to the decreased overall pressure in the system.

Since the calculations described refer nevertheless to comparatively short chains, it is doubtful if they fully reproduce the properties of polymers in which the chain length is usually very large. However, this is not so. The use of the MC method in combination with the procedures of the renormalisation group (RG) theory[43] has shown[44] that asymptotic behaviour is attained fairly rapidly for flexible chains with strong volume interactions. Even for $N = 8$–16, freely jointed non-intersecting chains satisfy the relation

$$\langle R^2 \rangle \propto N^{2\nu} \qquad (9)$$

where the critical index $\nu = 0.589 \pm 0.003$, which actually agrees with the limiting value (the best calculation carried out hitherto by the field theory method[45] for $N \to \infty$ yielded $\nu = 0.588 \pm 0.001$; the most reliable experimental result is $\nu = 0.586 \pm 0.004$, which has been obtained[46] for polystyrene with $M_w \leqslant 5.6 \times 10^7$). A criterion of asymptotic behaviour is the inequality $N \gg (b/\sigma)^6$, where $b$ is the chain length and $\sigma$ the effective rigid chain diameter. For the chains considered in numerical experiments,[34–42] this condition apparently holds, since in all cases $b/\sigma \cong 1$. For this reason, even what are at first sight very short chains should correctly reflect the equilibrium properties of high-molecular-weight polymers.

Thus computer simulation methods have shown that, in dilute solution a low-molecular-weight neutral solvent has only a weak influence on the conformation of a flexible polymer chain for the usual densities and pressures. The interactions of the chain units themselves play a more significant role. The approaches in which the solvent is excluded from explicit consideration in the computer modelling of the equilibrium properties of polymers and the solvent is only considered via the appropriate selection of the interaction potentials between units are therefore fully justified. If the effective potentials are such that the repulsive forces predominate in the interaction and the macromolecule swells, increasing thereby its volume relative to the θ-dimension $R_\theta (R_\theta \sim bN^{1/2})$, it is natural to assume that a thermodynamically effective solvent is modelled. On the other hand, if the coil is compressed relative to $R_\theta$ owing to the strong attraction of the units and passes to a globular state, then one models a solvent whose quality is inferior to that of a θ-solvent. Naturally in such a study the effective potentials have the significance of the potentials of the average interaction force, i.e. they determine the change in the free energy and not in the potential energy of the interaction.

Special problems arise in the computer modelling of polyelectrolytes, in which there are long-range electrostatic interactions within the chain. Charged flexible chains containing $N \leqslant 321$ units have been investigated by the MC method in spaces with $d = 3$–7 dimensions.[47] A non-shielded Coulombic potential has been used to describe the electrostatic forces. It was found that the index $\nu$ in Eqn.(9) is $\nu = 3/d$. This result is extremely unexpected, because it is in full agreement with the conclusions of the classical Flory theory[48] but shows a sharp discrepancy with the RG treatment,[43] which predicts that $\nu = 2/(d-2)$ for $4 < d \leqslant 6$. This can be seen from Fig.3, where the result of the computer calculation of $\langle S^2 \rangle$ is compared with the RG relation for a five-dimensional space. It may be that in the case of a long-range potential the chain length is insufficient for the complete realisation of the volume effects even with $N \cong 10^2$.

## 3. Dynamic Properties

In the study of dynamic properties, one usually calculates the diffusion coefficients and various autocorrelation time functions (AF) of the type $C(A, t) = \langle A(0).A(t) \rangle$ characterising under stationary conditions the correlation between the values of the function $A$ considered at time intervals $t$.

The translational diffusion coefficient $D$ is obtained by integrating the AF for the velocity $C(\mathbf{v}, t)$ by the Green–Kubo formula[22]

$$D = (1/3) \int_0^\infty \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle dt,$$

or by the Einstein formula

$$\lim [\langle \Delta r^2 \cdot (t) \rangle]_{t \to \infty} = 6tD + B,$$

where

$$\langle \Delta r^2(t) \rangle = \langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle$$

is the mean square displacement of the particle during time $t$ and $B$ a coefficient which determines whether the diffusion is more intense or weaker than a Markov process and the angular brackets denote averaging with respect to time and all the particles. The averaging range of $T$ should significantly exceed the relaxation time $t_0$ of the process considered because the error in the calculation of the normalised AF of the type $\langle A(0).A(t) \rangle / \langle A^2 \rangle$ for a given $t$ is $(2t_0/NT)^{1/2}[1 - \langle A(0).A(t) \rangle / \langle A^2 \rangle]$.

We shall now turn to small-scale and high-frequency movements (corresponding to times $\leqslant 10^{-0}$ s (error in Russian, Ed.) for real systems); information about such systems can be derived, for example, by the dielectric relaxation, polarised luminescence, NMR, EPR, etc. methods. This problem has been studied by the MD method.[37,38,49]

For a better understanding of the polymer effects, we shall consider primarily the simplest "molecule" of anisotropic shape made up of rigidly linked particles ("dumb-bell"), which moves in a liquid made up of non-bonded species. The mean square displacement of the centre of gravity of the dumb-bell is a linear function of $t$ with the exception of a short initial section—the inertial region, where $\langle \Delta r^2(t) \rangle \sim t^2$. As for a homogeneous system, the boundary between the inertial and diffusion regions is determined by the time $t \sim \gamma/m$, where $\gamma$ is the coefficient of friction of the moving particle. The rotation of the dumb-bell is also described by diffusional laws. This means that the rotational AF bond vectors b are given by the expression

$$\langle P_l[\cos \theta(t)] \rangle = \exp[-l(l+1)D_R t],$$

where

$$\cos \theta(t) = \mathbf{b}(0) \cdot \mathbf{b}(t)$$

is the cosine of the angle of rotation of b during the time $t$, $P_l$ is the $l$th Legendre polynomial, and $D_R$ the coefficient of rotational diffusion. We may note that the foregoing is valid for a bond length $b \gtrsim \sigma$, where the contribution of inertial movements to the relaxation of the AF is small. Otherwise a single characteristic time is insufficient for the description of the orientational AF.

There is a strong relation between the translational and rotational movements of an anisotropic particle in a liquid.[50] This feature can be manifested in spectroscopic experiments. In a dense medium the particle rotates faster the more rapid its translational movement. This correlation can be accounted for by the presence of a local structure in the liquid. For a constant density of the system, the coefficient $D$ for a dumb-bell increases linearly with temperature, which means that the local viscosity of the medium is determined primarily by the free volume.

Overall, analysis of the MD calculations permits the conclusion that the movement of an anisotropic particle in a solvent can by correctly described as the movement of a Brownian particle in a continuous viscous medium. The accuracy of such description increases with increased difference between the masses, dimensions, and shape anisotropies of the given molecule and the molecule of the medium. It must be specially emphasised that the translational movement of a particle and its rotation are, as it were, made up of a large number of small jumps and not of several large jumps. The diffusing particle interacts strongly with its environment under these conditions and its movement is a collective process. This idea was put forward by Frenkel'.[51] The MD method made it possible to elucidate certain fine details of molecular movements in dense media.

The study by the MD method of flexible chains in media made up of particles whose interaction is described by the Lennard-Jones potential [Eqn.(8)] has shown[49] that, for short times $t \lesssim 0.2\tau$, the units move as in the gas phase, while in the range $0.3 < t/\tau < 4$, so long as the displacement $\Delta r$ remains small compared with the characteristic chain dimension, we have $\langle \Delta r^2(t) \rangle \sim t^{\alpha}$, where $\alpha < 1$. A more detailed study[37] gave $\alpha \cong 1/2$. The manifestation of this unusual motion regime, which is absent for the free particles, is due to the inhibiting effects of skeletal bonds. The presence of branches induces additional inhibition: $\langle \Delta r^2(t) \rangle \sim t^{1/2}/k$, where $k$ is the functionality of the given monomer.[38] We may recall that the $\langle \Delta r^2(t) \rangle \sim t^{1/2}$ relation is predicted by the Kargin–Slonimskii–Rowse model of Gaussian subchains.[43] Naturally, for large values of $t$, the general diffusion law always holds, although the shift of the monomers is influenced by the chain length: $\langle \Delta r^2(t) \rangle t/N$.

A characteristic feature of the chains with rigid bonds is the increased velocity of the terminal chains compared with the internal chains (the difference is 10–10%).[52] This "hot end" effect is due to the differences in the number of degrees of freedom.

The relaxation of the spatial orientations of the bond vectors of a chain immersed in a solvent has been investigated.[37] Comparison of the results of the MD calculation with the analytical predictions of the viscoelastic Herst–Harris model showed that the relaxation of the mean cosine of the angle of rotation of the bonds [i.e. the orientational AF of the type $\langle \cos \theta(t) \rangle$] takes place in a real chain in virtually the same way as the relaxation of the equivalent quasi-elastic elements in the Herst–Harris model. A rigid chain bond then corresponds to an elastic element of the model and the mean angle between the elements of the viscoelastic model is close to the mean angle between the bonds. In addition, the relation between the mean cosines and mean squares of the cosines of the angles of rotation of the chain bond vectors is similar to the same relation for the individual dumb-bells diffusing in a viscous medium. In other words, the characteristic time of the orientational AF obeys with satisfactory accuracy the expression $t_1/t_l = l(l+1)/2$. However, the orientational AF of the bonds in the macromolecule do not reduce to a simple exponential relation with a single characteristic time $t_l$ and require for their description a fairly broad spectrum of relaxation times. The same conclusion has been reached also in modelling an individual chain by the BD method.[53] This fact is due to the interrelation between different movements in the macromolecule and reflects its chain structure and is not associated with the presence or absence of a solvent.

The general results of the MD calculations can be formulated as follows. The characteristics of the local movements of polymer chains in a low-molecular-weight solvent are close to those manifested in the movement in a continuous viscous liquid. The solvent behaves as a continuous homogeneous medium in relation to the dissolved macromolecule even when the dimensions of the solvent molecule and the chain are comparable. Consequently the MD method confirms the *a priori* postulates which are used in modelling the dynamics of polymers by the BD method, where the medium is regarded at the very beginning as a dense continuum and is not taken into account explicitly but only via the effective coefficient of friction $\gamma$ in the Langevin equation. Assuming that the chain units move like Brownian particles, it is natural to specify the parameter $\gamma$ on the basis of preliminary MD calculations. Because of this, there is no need in the BD method to solve the equations of motion for an enormous number of solvent molecules and it is therefore possible to increase significantly the observation time. This is the main advantage of the BD method. It is used, for example, in the study of the conformational *trans–gauche* transitions in polymers with barriers to internal rotation.[53,54] It has been established that the conformational rearrangements occur mainly owing to weakly correlated single barrier $T \rightleftharpoons G$ transitions and their rate is described by the relation $K \exp(-E^*/kT)$, which is close to the Arrhenius relation, where the activations energy $E^*$ differs little from the height of the potential barriers separating the rotational isomers $T$ and $G$. Cooperative transitions of the type GTT $\rightleftharpoons$ TTG and TTT $\rightleftharpoons$ GTG are observed much more rarely.

We shall now consider the movement of the chain as a whole. The autocorrelation function for the velocity of the centre of gravity of the coil has a complex form: after the rapid decrease to zero (during a time $t \cong 0.2\tau$ for $N = 9$), a region of negative values is observed.[39] This phenomenon is apparently associated with the small number of chain units and can be explained by the fact that the diffusing molecule, having collided with the shell of surrounding particles of the medium, undergoes a kind of "backward reflection". This is possible only when the local environment ("cell") around the molecule considered is retained during a certain period.

It is of interest to compare the AF for the dimensions of an isolated chain and a chain immersed in the solvent. Evidently in a viscous medium the relaxation processes are retarded. Indeed the relaxation times $R^2$ and $S^2$ of nine-unit chains suspended in a solvent exceed by more than an order of magnitude the corresponding values for an isolated chain.[39] The vector R connecting the terminal units relaxes most slowly, owing to the necessity for the reorientation of the entire chain. According to Grivtsov

and Mazo,[55] the distance $|\mathbf{R}|$ is an aperiodic function of time, undergoing individual relatively large fluctuations. On the other hand, regular pulsations, whose period increases in direct proportion to $N$, are characteristic of an isolated chain. An increase of temperature accelerates the decrease of AF. For $t = 10\varepsilon/k$, the AF for a freely jointed chain made up of nine units decrease to zero over a short period $t \lesssim \tau$ corresponding to approximately one vibration period of a pair of particles.[35]

The influence of attraction in a dilute solution has been investigated[41] and it has been shown that allowance for the attraction between all the system particles retards the decrease of the AF for dimensions.

An important question is the study of the dependence on the molecular weight of the characteristic times for the AF describing the relaxation of the polymer coil. The standard approach to the solution of this problem for an isolated chain (without hydrodynamic interaction) consists in using the MC method with its dynamic interpretation. However, in this case it must be emphasised that such calculations based on lattice models yield results which are determined to a large extent by the chosen mechanism of the movement of the chains and frequently lead to various kind of artefacts, including a very marked dependence of the maximum relaxation time of the coils $t_m$ on $N$: the non-lattice models are therefore preferable.

Using the MC method and the principles of dynamic scaling,[57] it has been shown,[56] in relation to non-intersecting annular molecules, that, as for the equilibrium properties, the asymptotic dependence of $t_m$ on $N$ is attained extremely rapidly (for $N \gtrsim 40$) and the exponent $\alpha$ in the relation

$$t_m \sim N^{\alpha} \qquad (10)$$

is close to 2.2. The same conclusion has been reached in modelling non-lattice non-intersecting chains ($N$ = 5–63) with the aid of the SMART algorithm.[20] It follows from Eqns.(9) and (10) that the formula $\alpha = 2\nu + 1$ holds with satisfactory accuracy. It is known that for Gaussian chains $\alpha = 2$.[43] In addition we may note that the above calculation[56] failed to reveal an appreciable difference in the dynamic behaviour of simple rings and their topological isomers—three-loop knots; for the same $N$, the times $t_m$ are almost identical.

The role of hydrodynamic interactions can be followed in the MD modelling of solutions or in the study of an individual chain on the basis of the corresponding algorithms based on Brownian dynamics. Calculations by the MD method of the autocorrelation functions for the dimensions of chain ($N \leq 20$) surrounded by the solvent have shown[36] that, for overall system densities $\rho \leq 0.3$, the AF are described by a simple exponential relation $\exp(-t/t_m)$ and the times $t_m$ satisfy Eqn.(10) for $\alpha = 2.2$. $t_m$ increases with increase in $\rho$.

A fairly unexpected result has been obtained[58] in the modelling by the BD method of hydrodynamic interactions. It was found that the ratio of the chain size $R$ to the hydrodynamic radius of the chain $R_H$ depend both on the coefficient of friction of the unit and on the number of units; on the other hand, in the theory $R/R_H$ = const.[43] It may be that the dependence of $R/R_H$ on $N$ can be accounted for by the insufficient length of the chains investigated ($N \leq 56$).

## III. SEMIDILUTE SOLUTIONS

### 1. Scaling and Computer Simulation

In a dilute solution the polymer coils are separated and only rarely come into contact, while their dimensions at $T > \theta$ are specified by Eqn.(9). The region of a "semidilute solution" $\rho^* \ll \rho \ll 1$, where $\rho^* \sim N/\langle R^2\rangle^{3/2}$ is the critical value of the average density of the polymer units $\rho$ at which the coils begin to overlap, can be determined from general considerations. It follows from Eqn.(9) that $\rho^* \sim N^{-4/5}$, i.e. for high values of $N$ the quantity $\rho^*$ is very small. In a semidilute solution the local density of the units should therefore undergo strong fluctuations. According to modern theoretical ideas,[43] the principal parameter of such a system is the correlation radius of the density fluctuations $\xi$—the correlation length, i.e. the distance $r$ over which the local density of the units $\rho(r)$ differs from the average value of $\rho$. The quantity $\xi$ thereby characterises the dimensions of the regions of inhomogeneity in the solution.

The use of the parameter $\xi$ constitutes the basis of an elegant and extremely clear phenomenological description—the so-called blob model. The idea is that, having increased the scale of the study, one passes from the usual formulation of properties in terms of the collective interactions of polymer units to the formulation of the same properties in terms of the interaction of blobs. A blob is defined as a section of the chain (subchain) made up of $N_\xi$ units with the average dimension $\xi$. In other words, the increase in scale consists in the replacement of the repeating unit whose size is $\sim\sigma$ by a subchain (blob) with the dimension $\xi$. Since the chains retain their individual properties for scales $r < \xi$, for sections made up of $N_\xi$ units, one can write, by analogy with Eqn.(9), $\xi \sim N_\xi^{\nu}$. On the other hand, for scales $r > \xi$, all correlations vanish by definition. Therefore a chain, which can be imagined to be divided into $n = N/N_\xi$ blobs, has overall the following Gaussian dimensions: $R \sim \xi n^{1/2} \sim N^{1/2}$.

The above data make it possible to express important characterstics such as $\langle R^2\rangle$ and $\Pi$ (osmotic pressure) in terms of $\xi$ or $\rho$. When $T > \theta$, we have in the general case for a $d$-dimensional space

$$\langle R^2\rangle \sim N\xi^{(2\nu-1)/\nu} \sim N\rho^{(2\nu-1)/(1-\nu d)}, \qquad (11)$$

$$\Pi/kT \sim \xi^{-d} \sim \rho^{\nu d/(\nu d-1)}, \qquad (12)$$

where $\nu$ enters into Eqn.(9) [or is formulated approximately as $\nu = 3/(d+2)$] and account is taken of the fact that $\xi$ is a decreasing function of the average density:

$$\xi \sim \rho^{\nu/(1-\nu d)} \qquad (13)$$

The above treatment is based on the extremely general hypothesis that in the region of strong fluctuations the thermodynamic and correlation functions are generalised homogeneous functions of their arguments. This hypothesis constitutes the essential feature of the so-called similarity or scaling hypothesis. According to this hypothesis, the transformation of the linear scale $\mathbf{r} \to \lambda\mathbf{r}$ (or, in terms of dynamic scaling, the frequency scale) with an arbitrary similarity parameter $\lambda$ leads to the situation where the fluctuating physical quantities $A(\mathbf{r})$ should also vary in a similar manner $[A(\lambda\mathbf{r}) \to \lambda^{\Delta}A.A(\mathbf{r})]$ with a similarity exponent $\Delta_A$. On the basis of the phenomenological scaling concept, it is easy to establish a relation between the critical exponents $\Delta_A$, provided that some of

them are already known. An example is provided by the power relations (11)–(13) formulated in terms of a single power exponent $\nu$. However, the calculation of the parameters themselves is a problem for microscopic theory.

One such approach, which takes into account the cooperative interactions in the system, is known as the theory of the mean (or self-consistent) field. The entire classical Flory theory of polymer solutions is based on this approximation.[48] In it, a uniform distribution of the densities throughout the system is assumed, i.e. it is assumed that the local density $\rho(r)$ coincides with the average value of $\rho$ over any distance. In this treatment $\langle R^2 \rangle$ is independent of $\rho$ and formulae (12) and (13) assume the forms $\Pi \sim \rho^2$ and $\xi \sim \rho^{-1/2}$.

The Flory theory proved to be extremely constructive, but, with increase of the experimental accuracy, data conflicting with it began to accumulate. This led to the appearance at the beginning of the 1970's of an alternative approach based on the fundamental postulate of the mathematical isomorphism of two systems: the polymer solution in the region of strong fluctuations and a magnetic material in an external field $H$ near the critical temperature $T_c$. It has been demonstrated rigorously[43] that there is an unambiguous correspondence between the "magnetic" and "polymeric" variables: $H \leftrightarrow \rho$ and $T/(T - T_c) \leftrightarrow N$ (or $N_\xi$). The field theory methods, which have been satisfactorily developed for magnetic materials, make it possible to calculate the critical indices at $|T - T_c| \to 0$ (or in polymer terms, $1/N \to 0$) and, by virtue of the analogy indicated between polymers and magnetic materials, these indices are automatically transferred to the polymer theory. In many cases they can be measured experimentally. This is in fact the aim of the computer experiment, whose evident advantage is the possibility of excluding the influence of extraneous factors such as the inhomogeneity of the chemical structure of the specimen and its polydispersity, the association of the macromolecules, etc. In the main, one solves problems designed to discover a measure of the deviation from the classical Flory theory, to refine the limits of applicability of the scaling relations (11)–(13) to the practically important region of the parameters $N$ and $\rho$, and to test the phenomenological relations between various critical indices resulting from their independent calculation.

The equilibrium properties of semidilute solutions are usually studied on a computer by the MC method. Two characteristic features of the modelling of such systems have been noted. On the one hand, there is the general problem of the modelling of long chains coupled with the need to incorporate a large number of geometrical conditions imposed by the skeletal angles and bonds. Generally speaking, for fixed geometrical parameters, it is not possible to consider the independent movements of an individual chain unit while the remaining chains are stationary, as is done in the Metropolis scheme for a system of "dissociated particles", where only one particle selected at random migrates at each step. For chains with rigid bonds, this type of movement can be organised in three artificial ways. If the chain is modelled by a broken line on a cubic lattice, there is a possibility of jumps of elementary sections in the form of "corners" (fragments made up of two bonds) or "collars" (fragments made up of three bonds); this is the model of Verdier and Stockmayer.[59] In the "slithering snake" algorithm[60] the terminal unit is "torn off" at each step and is reattached in a random manner to the opposite end of the chain. This algorithm is equally applicable to lattice and continuous models. Finally, if the skeletal angles are not fixed, then any internal unit $i$ can be caused to pass to a new state by rotating it by random angle around an imaginary axis connecting the neighbouring $i - 1$ and $i + 1$ units (the Baumgärtner model).[61] In all cases the possibility of the transition between successive configurations is defined by Eqn.(1).

Naturally, the use of smooth potentials (and not $\delta$-functions) for the description of the chain structure makes it possible to abandon artificial mechanisms of motion. The calculations, mentioned above, by means of the SMART algorithm[19–21] lead precisely to this type of model. In addition, without any *a priori* ideas about the mechanism of motion, it is possible to model by the MC method also chains with rigorously fixed bonds (angles), provided that one resorts to correcting algorithms (of the type of SHAKE), which are used in molecular dynamics. However, it is so far not clear whether such schemes have advantages over traditional schemes.[59–61].

On the other hand, by virtue of the fact that in the modelling of semidilute solutions without an explicit allowance for solvent molecules the average density of the test substance in the system is fairly low ($\rho \ll 1$), it becomes possible to use computational methods based on the generation of an *ensemble* of statistically independent configurations, where the chains in each configuration are built up from the beginning to the end by the successive increase in the number of units.[2–4] Polymer solutions constitute an extremely rare example of physical systems for which interesting problems, susceptible to solution by the method of independent samples, exist. Naturally, for $\rho \cong 1$, this method is generally useless. However, in those cases where it can be applied, it is virtually the optimum method.

## 2. Monodisperse Systems: Concentration Relations

*The correlation length.* Having specified around each chain unit a sphere with a radius $r$ and having found the number of units $N(r)$ in a volume $V = 4/3\pi r^3$, it is possible to calculate the local density $\rho(r) = \langle N(r) \rangle / V$ after averaging with respect to all the units of the system and with respect to all the configurations generated. For low values of $r$, the internal density of units makes an overwhelming contribution to $\rho(r)$; in essence, it determines the quantity $\xi$, which is a result of the numerical solution of the equation $\rho(r) = \rho$, which is satisfied by the condition $r = \xi$.

The concentration variation of $\xi$ has been studied by the MC method for continuous chains with free internal rotation,[62,63] for lattice chains,[64] and for a solution of polyethylene.[65] It has been shown that, for small values of $\rho$, the quantity $\xi$ is comparable to $\langle R^2 \rangle^{1/2}$ and is naturally independent of $\rho$. If $\rho > \rho^*$, then $\xi$ diminishes with increase of $\rho$, which indicates a weakening of the density fluctuations. It has been established[62,63] that for chains in a volume ($d = 3$) and on a plane ($d = 2$), the calculated data are described satisfactorily by Eqn.(13). Thus, for a system of 40-unit chains in the region $0.05 \leqslant \rho < 0.37$, the exponent $x_d$, which defines the dependence of $\xi$ on $\rho$ in Eqn.(13), was found to be $-0.65 \pm 0.04$ for $d = 3$ and $-1.17 \pm 0.09$ for $d = 2$. For chains on a cubic lattice, the quantity $x_3 = -0.71$ has been obtained.[64]

An important result of the study of Khalatur et al.[65] is the demonstration that $\xi$ is independent of $N$ for $\rho > \rho^*$. This conclusion also follows from de Gennes' theoretical study.[43] When $\rho \to 1$, the quantity $\xi$ approaches the size of the chain unit. It has been established[65] that, for polyethylene chains at a density equivalent to ~0.7 of that of the pure liquid, we have $\xi \cong 0.6$ nm.

These data can be correlated as a result of an experiment[66] where a decrease of $\xi$ from 10 to ~1 nm has been observed in neutron scattering by deuteriated polystyrene for $\rho = 0.01-0.15$. The second value is close to the length of Kuhn's segment, which is 1.7 nm for polystyrene.

A semidilute solution in contact with an impermeable wall has been investigated[67] by the MC method and the distribution of the densities of units $\rho(z)$ in the direction of the normal $z$ to the wall has been calculated. The quantity $\xi$ was found from the condition $\rho(z) = \rho$. Analysis confirmed the power relation (13) and the corresponding exponent was found to be $x_3 = -0.74 \pm 0.15$, which in fact does not differ from the values quoted above. Thus the concentration variations of $\xi$ are virtually the same for different ways of determining it. In all cases the values of $x_d$ found agree well with the theoretical values.[43] In fact, if the fairly accurate approximation $\nu = 3/(d + 2)$ is adopted for the index $\nu$, then we have from Eqn.(13) $x_3 = -3/4$ and $x_2 = -3/2$; in the Flory theory $x_2 = -1/2$.

The correlation length can also be estimated by calculating the intrachain contribution to the static structure factor. Such calculations have been performed by the MC method[68] for 201-unit chains on a lattice. It was found that, for $\rho = 0.344$, the quantity $\xi \cong 10$ when expressed in units of the length of the step in a tetrahedral lattice $b = 3^{1/2}$ and the average number of units in the blob has been estimated as $N_\xi \cong 16$.

Thus computer experiments confirmed the possibility of describing a semidilute polymer solution on the basis of the blob model. It is also significant that the comparatively short chains considered, consisting of several tens or hundreds of statistical segments, correspond to the range of molecular weights of practical importance.

*Average dimensions.* The dependence of $\langle R^2 \rangle$ on $\rho$ was first investigated[69] by the MC method for continuous chains consisting of 15 and 20 units. It was found that, with increase of $\rho$, the coils swollen in an effective solvent contract. Analogous conclusions have been reached in a large number of subsequent publications. Sariban et al.[70] also modelled a system under the conditions of a thermodynamically poor solvent at $T < \theta$. For this purpose, they attributed an attraction energy $\varepsilon = -0.5\ kT$ to pairs of units which have approached one another, which led to the contraction of the coils in a dilute solution relative to $\theta$-dimensions. For such a system, the opposite tendency was observed with an increase in $\rho$: compressed coils became uncoiled and their dimensions approached $\langle R_\theta^2 \rangle$.

A computer study of the functional relation between $\langle R^2 \rangle$ and $N$ showed that,[68] for sufficiently long chains ($N \sim 200$) in an effective solvent, the linear relation $\langle R^2 \rangle \sim N$, corresponding to Gaussian chains and agreeing with Eqn.(11), holds already for $\rho = 0.2$. The same results have also been obtained[71] for a two-dimensional system.

A critical analysis of computer studies of the concentration variation of chain dimensions has been carried out.[72-74] Such a relation can be usefully considered using the scaling variable $X = \rho N^{d\nu-1} \sim \rho/\rho^*$, which provides a measure of the overlap of the coils. It has been noted[73,74] that in the majority of the determinations of the power exponent in Eqn.(11) systems made up of insufficiently long chains have been used. This yielded results differing from the theoretical values. Indeed, for Eqn.(11) to hold it is necessary that the marked inequality $\rho \gg \rho^*$ should obtain. In terms of the variable $X$, this is equivalent to $X \gg 1$. However, since the range of variation of $\rho$ is always limited, the condition $X \gg 1$ is attained only for very long chains whose computer simulation is difficult for technical reasons. The authors[75] therefore proposed another approach. It follows from scaling considerations that in a general form the quantity $\langle R^2 \rangle$ should satisfy the relation

$$\langle R^2 \rangle \sim N^{2\nu} \cdot Y^{(2\nu-1)/(1-\nu d)},$$

where $Y = \rho/\tau\rho^*$ and $\tau = (T - \theta)/\theta$ is the relative difference between the temperature and the $\theta$ point. Clearly, for a fixed value of $Y$, an improvement in the quality of the solvent (i.e. an increase of $\tau$ leads to an increase of the ratio $\rho/\rho^* \sim X$. Consequently, by intensifying the volume interactions, it is possible to achieve the condition $X \gg 1$ without increasing $N$. In a computer experiment, it is sufficient for this purpose to impart a statistical weight $\omega > 1$ to the units in contact. The corresponding calculations[75] led to the conclusion that, even for comparatively short chains ($N = 40-61$) with $\omega = 0.9$, the power exponent in Eqn.(11) is $-0.212 \pm 0.050$, which is close to the theoretical value of $-1/4$ for three-dimensional systems.[43]

The lattice model of a polyelectrolyte solution has been studied[76,77] by the MC method. An individual non-intersecting chain made up of $N = 16$ or 64 units, some of which carried a unit charge, was placed in a cell with mobile counterions. Each counterion also had a unit charge and was regarded as an occupied lattice site. The interaction between the charges was described by a non-shielded Coulombic potential. Using the local jump method,[59] the authors investigated the dependence of the chain size on the fraction of charged units $p_e$ and the average density of units, which was varied by altering the volume of the computational cell for fixed values of the remaining parameters. The calculation showed that the chain swells with increase in $p_e$. Consequently the environment made up of counterions, arising around the chains, cannot compensate for their electrostatic repulsion. This effect is most pronounced in a dilute solution (i.e. at a low ionic strength), where the total electrostatic energy is positive and the form of the polyion is close to being rod-like. The decrease in cell size modelled the increase in ionic strength. When the Debye radius is less than the chain radius $R$, the total electrostatic energy becomes negative and the polyion assumes the form of a coil. Under these conditions, the role of electrostatic interactions is insignificant compared with the "usual" volume interactions.

*Interaction of coils and osmotic pressure.* In dilute solution, the virial expansion

$$\Pi/kT = C/N + A_2C^2 + \ldots \qquad (14)$$

where $C = \pi\sigma^3\rho/6$ and $A_i$ is the $i$th virial coefficient, holds for $\Pi$. On the other hand, one can write for an arbitrary concentration[22]

$$\frac{\Pi V}{mkT} = 1 - \frac{1}{6kT} \cdot \frac{mN^2}{V} \int_0^\infty 4\pi r^2 g(r) \frac{\partial f(r)}{\partial r} r\,dr, \qquad (15)$$

where $m$ is the number of chains in the system, $g(r)$ is the "intermolecular component" of the radial distribution function of the unit, and $f(r)$ is the interunit potential.

The temperature variation of $A_2$ has been investigated[78,79] for lattice chains and the inversion of the sign of $A_2$ (the $\theta$ point corresponds to the equality $A_2 = 0$) was considered. It was found that the critical energy for a single contact between units $\varepsilon_0 \sim 1/T$, for which $A_2(\varepsilon_0) = 0$, depends on the chain length and differs for each $N$ from the value of $\varepsilon_0$ at which the swelling of the coils ceases.[80] The quantity $\varepsilon_0$ approaches its limiting value $\varepsilon_0^\infty$ as $\varepsilon_0(N) = \varepsilon_0^\infty(1 - N^{\theta-1})$.[80,81] Thus, in the case of finite chains one should speak of a $\theta$ region rather than of a $\theta$ point. We emphasise that the concept of the $\theta$ region was first introduced precisely on the basis of the analysis of the results of a computer calculation[82] and Khokhlov subsequently achieved a rigorous physical justification of this concept.[83]

The quantities $\Pi$ and $A_2$ are linked directly to the pair correlation function for the interaction of coils $G(h)$, which determines the probability of finding them at a distance $h$ from one another. The function $G(h)$ was calculated by the MC method.[84-86] The fundamental result of the studies of Khalatur and co-workers[85-87] has been the demonstration of the fact that, in an effective solvent, the probability of encountering conformations with a marked overlapping of the coils is significantly different from zero even on extrapolation to $N \to \infty$. On the other hand, the classical Flory–Krigbaum theory[48] predicts a zero probability of such states for chains with an excluded volume. An explanation of the results of the computer experiments and of the deficiencies of the Flory–Krigbaum theory has been given on the basis of simple scaling considerations.[85,86] These conclusions were later confirmed more rigorously using the renormalisation group method.[88] Sharp differences from the Flory–Krigbaum theory are also observed for the $\theta$ region.[4,89]

The concentration variation of $\Pi$ has been investigated for an athermal system[90-93] also taking into account the interunit attraction.[94] We may note that, when the units are modelled by rigid spheres with a diameter $\sigma$, then Eqn.(15) transforms into the simple expression

$$\Pi V/mkT = 1 + 4NCg(\sigma),$$

where $g(\sigma)$ is the value of $g(r)$ at the point of contact for $r = \sigma$ and the product $C.g(\sigma)$ gives the average number of contacts referred to one unit.

Calculations for non-lattice chains with $N \leq 40$ showed[93,94] that the relation $\Pi \sim \rho^x$, where $x = 2.44$, holds in an effective solvent. From Eqn.(12) with $d = 3$, we have $x_3 = 9/4$. On the other hand, in the Flory–Huggins theory[48] $\Pi \sim \rho^2$. The difference is due to the fact that the Flory–Huggins theory[48] neglects the important correlation effects arising due to the chain-to-chain binding. For the osmotic isothermal compressibility, it was found[94] that $\rho^2\beta_T \sim \rho^{-0.3}$, while in the case where correlations were not taken into account we have $\rho^2\beta_T = \text{const}$.

The possibility of describing the relation $\Pi(\rho)$ on the basis of the integral equations of the theory of liquids (the Percus–Yevick and hyperchain approximations) has been considered.[95] It was found that in the region $\rho > \rho^*$ these approximations give an unduly low pressure compared with the computer calculations. Two-dimensional systems have also been simulated.[92,93] $\Pi \sim \rho^{3.07}$ has been obtained[93] for an athermal system. It follows from Eqn.(12) that $\Pi \sim \rho^3$. In addition, in the same study it was discovered that $\Pi \sim \xi^{-d}$.

Thus the computer simulation of semidilute solutions of flexible chains in an effective solvent generally confirms the validity of the scaling method and yields critical indices close to those obtained in modern theories. On the other hand, a systematic deviation from classical ideas has been observed.[48]

### 3. Polydisperse Systems

Real polymer systems almost always exhibit a particular degree of polydispersity. The role of this factor has been analysed using scaling relations.[96] The behaviour of a flexible chain made up of $N_1$ units surrounded by units having the same chemical composition but made up of shorter chains with $N_2$ units has been considered. It was established that, when $N_2 \lesssim N_1^{1/2}$, then, in an effective solvent with an overall density $\rho > \rho^*$, the size of long chains $R_{1,2}$ in a mixture with short chains should increase compared with the size $R_1$ of the same chains at the same density but in the absence of short chains. The relative swelling coefficient

$$\beta = \langle R^2_{1,2}\rangle / \langle R_1^2\rangle$$

depends both on the ratio of $N_1$ and $N_2$ and on the density $\rho$.

Continuous non-intersecting chains with free internal rotation have been studied[97] by the MC method. In the first place the concentration variation of $\langle R_1^2\rangle$ was obtained for a monodisperse solution of 61-unit chains. Some of these chains (50%) were then replaced by shorter chains with $N_2 = 5$. The density was then defined as $\rho = (m_1N_1 + m_2N_2)/V$, where $V$ is the volume of the computational cell and $m_1$ and $m_2$ are the numbers of chains of different kinds in the cell. In a monodisperse system, the quantity $\langle R_1^2\rangle$ also decreases with increase of $\rho$. The contraction of the coils has been observed also in a two component system made up of chains of two kinds. However, the decrease of $\langle R^2_{1,2}\rangle$ begins later than that of $\langle R_1^2\rangle$ (for $\rho/\rho^* \gtrsim 2$). It has been shown that, for the same density, $\langle R^2_{1,2}\rangle > \langle R_1^2\rangle$. Consequently the relative swelling coefficient $\beta > 1$. In other words, the replacement of some of the long chains by short chains entails the swelling of the longer chains, which is equivalent to an improvement in the quality of the solvent for them. Naturally, with increase of $\rho$, the absolute size of the coils in an effective solvent always diminishes, although the ratio $\beta$ increases in proportion to $\rho$. According to Pletneva et al.,[97] such an increase continues for the system investigated up to $\rho \cong 0.2$, after which $\beta$ virtually ceases to vary.

The computer modelling of a polydisperse system has also been carried out using the SMART algorithm.[98] A mixture of flexible chains with $N_1 = 70$ and $N_2 = 5$ (the cell with $\rho = 0.3$ contained ten 5-unit chains and one 70-unit chain) and it was found that the quantity $\langle R^2\rangle$ for a "trial" 70-unit chain in a medium made up of short chains increases by a factor of 1.1 compared with the homogeneous system, which is close to the results of Pletneva et al.[97] The concentration variation of $\beta$ has not been investigated.[98]

It is noteworthy that the results of computer calculations considered above[97,98] agree qualitatively with the experimental data[99] for neutron scattering by mixtures of polydimethylsiloxanes.

## IV. POLYMERIC LIQUIDS

### 1. Conformational Structure of Macromolecules

In the computer study of macroscopically isotropic (liquid, amorphous) polymers two questions are usually considered: (1) in what way does the local structure of a polymeric liquid made up of macromolecules with a large number of chemical bonds differ from the structure of a simple low-molecular-weight liquid and (2) how the chain conformation in the block differs from that in a dilute solution.

In most investigations of this field by the Monte Carlo method calculations have been made of the dimensions of the macromolecules represented by the simplest general models on lattices or in continuous space. Summarising the results obtained, one may say that, regardless of the model employed, the dimensions of flexible non-interacting chains in a block with a density $\rho \gtrsim 0.6$ are close to the $\theta$ dimensions. The dependence of $\langle R^2\rangle$ on the molecular weight is the same as for immaterial Gaussian chains, i.e. $\nu = 1/2$ in Eqn.(9). These conclusions confirm the so-called "Flory theorem".[48] This type of behaviour is a consequence of the fact that, for $\rho \cong 1$, the local density of the units hardly differs from the average value for the systems: the density fluctuations are therefore small and the treatment within the framework of the approximation of an average molecular field becomes valid.

Since the end of the 1970's, numerical experimental methods have been used vigorously in the study of more complex systems: liquid n-alkanes and polyethylene. An undoubted advantage of such systems is the possibility of a direct comparison of the calculated results with experimental data. On the other hand, the combination of computer methods, physical experimental methods, and analytical theory leads to the best understanding of the problem under consideration.

The MC method has been used[100–105] for the modelling of hydrocarbon chains in the melt. For each molecule of the system, account was taken of the chemical structure and of the hindrance and interdependence of the internal rotations. The interaction of chemically non-bonded groups was described by the Lennard-Jones potential [Eqn.(8)], whose parameters were selected on the basis of experimental data. Chains containing between 8 and 30 carbon atoms were studied;[100,101] longer chains (up to $C_{101}$) were examined in other studies.[102–105] The calculations showed that, for a density $\rho \gtrsim 0.7$ (relative to the density of the pure liquid), the chain sizes reach a constant value and depend only on the temperature and chain length but not on $\rho$. The mean square radii of inertia $\langle S^2 \rangle$ found for the melt are compared in Fig.4 with the corresponding values measured experimentally by the small-angle neutron scattering method.[106–108] In all cases an entirely satisfactory agreement between the results is observed. On the other hand, the values of $\langle S^2 \rangle$ for the chains in the block are close to the values of $\langle S_\theta^2 \rangle$ calculated analytically by the method of generating matrices for isolated chains without volume interactions. Consequently hydrocarbon chains in the melt are coiled up to form statistical coils. It is important to note that two series of independent calculations, i.e. those of Vacatello et al.[100] and Avitabile and Tuzi,[101] on the one hand, and those of Khalatur and co-workers,[102–105] on the other, carried out by means of different algorithms and on different computers, yielded virtually identical results.

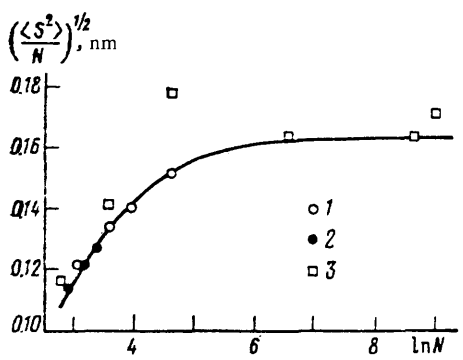



**Figure 4.** Dependence of $\langle S^2 \rangle$ for polyethylene chains in the melt on the number of carbon atoms $N$: 1) and 2) results of MC calculations from Refs.102–105 and 101 respectively; 3) experiment;[106–108] continuous curve—analytical calculation.

The problem of the mechanism of the transitions between the *trans*($T$)- and *gauche*($G$)-rotational isomers occupies an important place in the computer modelling of polymers. Naturally, for the solution of this problem it is necessary to consider realistic models. In this respect, the polyethylene oligomers are again the most convenient. The results of the molecular-dynamic calculations for liquid n-butane and n-decane[109–111] can be summarised as follows.

For liquid n-butane near the boiling point (292 K), a slightly increased fraction of the *gauche*-isomers ($p_G$) with respect to the C–C bonds is observed as compared with the gas phase: $p_G = 0.46$ in the liquid and $p_G = 0.34$ in the gas. The average $T \rightleftharpoons G$ transition time is ~10 ps. Modelling of liquid n-decane (27 molecules at 481 K) over 19 ps showed[111] that the average time interval $\Delta t$ between conformational transitions is ~2.1 ps. The fractions of the *gauche*-isomers with respect to different C–C bonds and the times $\Delta t$ are listed in Table 1. The relaxation of the chain as a whole takes 2–4 ps. This period is sufficient for the occurence of ~15 *trans–gauche* transitions. It has been shown[111] that the local conformation of n-decane is almost fully determined by intramolecular interactions.

More detailed calculations of the rotational-isomeric composition have been performed for liquid polyethylene oligomers by the MC method.[103,104] Not only the contents of the individual $T$- and $G$-isomers but also the contents of the various combinations of the *TT*, *GG*, *TG*, *TTT*, etc. types have been determined. We may note that it is only comparatively recently that we have learnt to extract such data from infrared and Raman spectra. Comparison of the results of computer modelling[103,104] for liquid $C_{21}$, $C_{51}$, and $C_{101}$ hydrocarbons with infrared spectroscopic data and the results of analytical calculation for unperturbed chains has shown a good quantitative agreement in all cases. This demonstrates that the local conformational structure of flexible chains in the block also differs little from the structure of a Gaussian coil.

The factors enumerated above constitute the most convincing evidence for the validity of the "Flory theorum" which has been produced by computer experiments.

## 2. Correlation in Liquid Polymers

We have already spoken of the correlation radius for density fluctuations; according to the results of the MC calculation,[65] $\xi < 1$ nm for liquid hydrocarbons. Calculations of the radial distribution functions[100] also show that $g(r) \cong 1$ at $r \gtrsim 0.7$ nm. The first $g(r)$ maximum in a hydrocarbon liquid, corresponding to the first coordination sphere, has been found at 0.4 nm, which agrees well with experimental X-ray diffraction data. In addition, the correlation function for the orientations of intermolecular pairs of C–C bonds has been determined[100] and it has been found that the orientational correlation disappears completely already at distances greater than 0.5 nm. An analogous result has been obtained[112] by the MD method for polyethylene having a density of 774 kg $m^{-3}$. At $r \lesssim 0.5$ nm, a weak tendency towards a perpendicular arrangement of segments has been observed. It has been established that even at $\rho > 0.5$ and even more so in the block state the polymer coils overlap almost completely.[87,113]

The question of the interpenetration of the coils on a plane has not been fully elucidated as yet. The available results of computer calculations are not unambiguous. Baumgärtner's data[114] indicate a tendency of two-dimensional coils towards segregation, which agrees with the hypothesis put forward by de Gennes.[43] However, this conclusion conflicts with other computer experiments[67,115] and theoretical studies[85,86] within the framework of the scaling method.

The relaxation behaviour of hydrocarbons in the melt has been investigated by the MD method.[109–111] Calculations[111] of the autocorrelation functions for the coil sizes in liquid n-decane have shown (Fig.5) that the AF for $S^2$ and $R^2$ decrease to zero over a period of ~1.5$\tau$ (2–3 ps). Consequently, despite the high viscosity of the medium, the coil sizes relax fairly rapidly. When the strong attraction of

the units is taken into account in the calculation, the rate of decrease of the AF diminishes[116] but to a much lesser extent than for a chain in a dilute solution. It is of interest to note that the AF calculated[111] by the MD method could be reproduced almost quantitatively by the method of Brownian dynamics for an individual chain with an appropriate choice of the coefficients of friction for the methylene group.[28] This result is also illustrated in Fig. 5. Naturally, the simulation of a dense system by a single macromolecule in the BD method is not suitable for the investigation of phenomena associated with topological effects arising owing to the intertwining of the chains in the liquid polymer. Such phenomena include the diffusion of the chains, which will be considered in the next Section of this review.

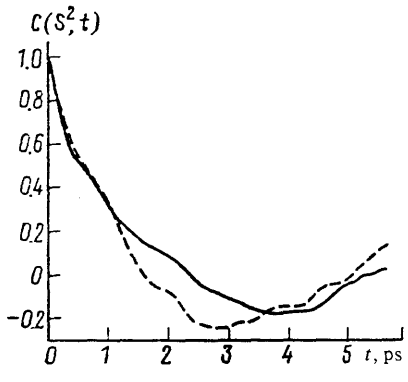



Figure 5. The autocorrelation function of the square of the radius with inertia of the n-decane chain.[111] Continuous curve—MD calculation for the melt; dashed curve—calculation by the method of Brownian dynamics for an individual chain.

Table 1. The fractions of the *gauche*-isomers relative to C–C bonds and the *trans-gauche* conformational transition times in liquid n-decane at 481 K.[111]

| No. of the C–C bond in the chain | $p_G$ | $\Delta t$, ps |
|---|---|---|
| 2 and 8 | 0.45 | 1.9 |
| 3 and 7 | 0.36 | 2.1 |
| 4 and 6 | 0.34 | 2.4 |
| 5 | 0.44 | 1.7 |

Naturally, in contrast to low-molecular-weight liquids, in liquid polymers there are correlations of a special kind due to the strong (chemical) bonds between neighbouring units in the chain. The role of these correlations can be traced by calculating the Van Hove spatial-temporal correlation function $G(r, t)$ (its Fourier transform defines the differential coherent scattering cross-section).[22] This function can be conveniently divided into two parts:

$$G(r, t) = G_d(r, t) + G_s(r, t),$$

where $G_d(r, t)$ is the density of the probability of observing any other species at time $t$ and a distance $r$ from the given species, while $G_s(r, t)$ is the density of the probability of observing the same species. We may note that $G_d(r, t)$ describes the evolution of the radial distribution function in time and $G_d(r, 0) \equiv g(r)$. The calculations of $G_d$ and $G_s$ were performed by the MD method for a system made up of 20 flexible 16-unit chains at $\rho = 0.8$.[117] The interaction of the units was described by the repulsive component of the potential defined by Eqn. (8). Fig. 6 presents the functions $g(r)$ and $G_d(r, t)$ at different times. The high first peak (with a height of ~11) on the $g(r)$ curve at $r = 1$ corresponds to the closest (bound) monomers in the chain separated by bonds of different lengths. The subsequent maxima correspond to different coordination shells. In the region $r > 4$ the oscillations in the $g(r)$ have almost completely decayed, which is also characteristic of simple low-molecular-weight liquids.[22] Thus the principal specific features of the equilibrium structure of a liquid polymer consist in the presence of an intense "valence" peak on the $g(r)$ curve.

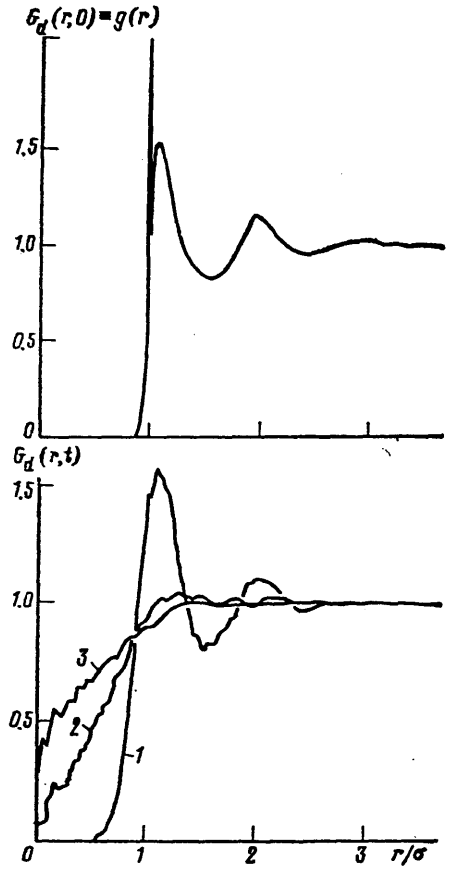



Figure 6. Radial distribution function of the density of the particles and the Van Hove function for a polymeric liquid at different times t: 1) $0.2\tau$; 2) $\tau$; 3) $2\tau$.

It might have been expected that many bonds in the chains should influence strongly the dynamics of the decomposition of the pair density correlations. However, Fig. 6 showed that, even for $t > 0.2\tau$, a barely perceptible trace remains of the "valence" peak on the $G_d(r, t)$ curve. With increase of $t$, other peaks spread and gradually disappear. Nevertheless, even at $t \cong \tau$, the short-range order cell, made up of particles in the first coordination sphere, is appreciable.

The region of forbidden volume persists for an even longer period for low values of $r$. However, during a period $t > 4\tau$, the initial $G_d(r, t)$ structure decomposes to a large extent and at $t \gg \tau$ we have $G_d(r, t) = 1$ for all distances, i.e. any relative positions of the particles are equally probable. The autocorrelation function $G_s(r, t)$, describing the self-diffusion of the particles, then obeys the Gaussian law.

### 3. Reptational Movement

De Gennes[118] proposed a heuristic model, which has been called the "reptation model", for the description of the diffusion of flexible chains in dense media. The movement of the chain can be clearly represented using the concept of an effective tube: it is assumed that at any instant each chain is, as it were, enclosed in a "tube" made up of the steric hindrance generated by other chains in the system. The macromolecule diffuses within this tube as a result of local conformational rearrangements—"defects", which migrate preferentially along the chain contour. Such low-scale (in fact one-dimensional) movement is the basis of the reptation model.

One of the maximum characteristic times of the process is $t_R \sim N^3$, during which the chain moves along the tube over a distance of the order of its contour length. At $t \sim t_R$ the movement of the chains is described by the relation $\langle \Delta r^2 \rangle \sim (t/N)^{1/2}$. For times much shorter than $t_R (t \leq t_R/N)$, when the average displacement of any unit $\langle \Delta r^2 \rangle^{1/2}$ is comparable to the effective tube diameter $d_T$, a special "local reptation" regime should be observed, in which $\langle \Delta r^2 \rangle \sim t^{1/4}$. Finally, for very short times $t$, the movement of the unit is controlled solely by the intrachain bonds and not by intermolecular interactions, which corresponds to the usual Rouse model, i.e. $\langle \Delta r^2 \rangle \sim t^{1/2}$.

The experimental observation of reptations in liquid polymers is extremely difficult. For this reason, there are as yet no direct unambiguous data confirming or disproving the postulated reptation mechanism. In a series of recent studies,[68,98,119–123] an attempt has been made to observe reptation by the dynamic MC method.[59,61] However, in the modelling of melts this could not be done. In our view, the failure can be accounted for by two causes. Firstly, in the above studies insufficiently dense systems ($\rho < 0.7$) were considered. Since $\langle \Delta r^2 \rangle^{1/2}$ should be close to $d_T$ for the manifestation of reptational movement, it follows that, when account is taken of the estimate $d_T \cong (\sigma\rho)^{-1/2}$ ($\sigma$ is the diameter of the monomer), it becomes clear that for low $\rho$, it is difficult to reproduce the required regime in a numerical experiment. Secondly, in modelling polymers by the dynamic MC method, the movement of the macromolecule is achieved as a result of successive rearrangements of short sections of the chains. It is then found that, for chains with volume interactions and rigid bonds, the rate of migration of units along the chain contour is very low. The reptation mechanism is therefore hardly realised. This has been confirmed by the results of a study[121] where the reptational movement has been observed only after assuming the overlapping of the monomers within the same chain. For this reason, one cannot regard as satisfactory also the calculations[122] for an individual macromolecule without exchange interactions, moving within a regular network of obstacles modelled by a regular cubic lattice. Furthermore, the appearance of reptational movement in a medium with regular obstacles is in general doubtful.

It has been reported[68,98,119,120] that it has been possible to observe a transition from the Rouse regime ($\langle \Delta r^2 \rangle \sim t^{1/2}$) to the reptational regime ($\langle \Delta r^2 \rangle \sim t^{1/4}$) after the movement of all the chains in the melt has been "frozen" with the exception of one trial chain. We should like to draw attention to the lack of justification of this conclusion. In fact, in the random appearance of a "frozen network" there is an extremely high probability that a mobile chain is incorporated in a cell closed on all sides (and not in a tube open at two ends), which naturally causes a sharp retardation of the movement.

The reptation of chains in the melt has also been investigated by the MD method.[117] This method is free from the above disadvantage characteristic of the MC method and it therefore provides a more objective description of the dynamic behaviour. The mean squares of the displacements of the units $\langle \Delta r^2 \rangle$ and the orthogonal components of the movement along the chain contour (the tangential component $\Delta r_\parallel$) and across the contour (the normal component $\Delta r_\perp$) have been considered[117] for a dense system of 20 flexible chains ($N = 16$, $\rho = 0.8$). Clearly

$$\langle \Delta r^2 \rangle = \langle \Delta r_\parallel^2 \rangle + 2\langle \Delta r_\perp^2 \rangle$$

and the ratio

$$Q = \langle \Delta r_\parallel^2 \rangle / \langle \Delta r_\perp^2 \rangle$$

is therefore always unity for isotropic movement. In order to make a comparison with the melt, an individual chain has also been considered.[117] The calculation showed that, owing to the presence of rigid bonds, the movement of the units of an individual chain in the tangential direction is suppressed and the normal component predominates, so that always $Q \leq 1$. An analogous behaviour is characteristic also of chains in the melt for short times $t \leq \tau$. The dynamic properties are then determined solely by the chain structure of the macromolecules and not by their interaction. However, for $t \geq 1.2\tau$, where each unit in the melt has sufficient time to traverse a fairly long distance $\sim d_T$, the obstacles offered by the surrounding chains, which arise during the movement in the transverse direction, force the units to migrate predominantly along the chain contour, as a result of which $Q > 1$. This picture can be readily traced in Fig. 7. Naturally, for very long times, the movement must be isotropic.

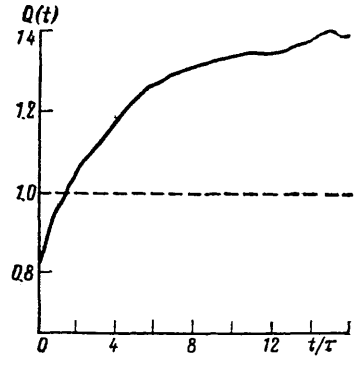



**Figure 7.** Time variation of the function $Q(t)$ defining the ratio of the shifts of the polymer chains along and across the chain contour. The calculation was performed by the method of molecular dynamics for a dense polymeric liquid.[117]

Thus a dynamic numerical experiment has shown that in a polymeric liquid there exists a preferential type of movement of the chain units along the chain contour. This

movement is solely determined by a specific interchain interaction and can be identified with local reptations in the melt. From the general standpoint, this situation is fairly unusual: in a system having an isotropic structure, there exists a local anisotropy in the movement of the particles.

## V. PARTLY ORDERED SYSTEMS

### 1. Liquid Crystal Polymers

The fields involving the practical application of polymeric liquid crystals have expanded sharply in recent years and new prospects have arisen for their further application. These factors stimulated theoretical studies of the conditions governing the appearance and physical properties of liquid crystal systems.

The possibility of transition to a liquid crystal phase is associated with the rigidity of the polymer chain, characterised by the statistical Kuhn segment $A$, rather than by its great length. If $A \gg \sigma$ ($\sigma$ is the chain diameter), then, under certain conditions, orientational ordering may take place. Polybenzamide, poly-(benzyl glutamate), and cellulose esters are typical examples of mesogenic macromolecules for which $A \gg \sigma$.

There exist two main approaches to the theoretical description of the orientational ordering of macromolecules: the Onsager method,[124] in which the virial expansion of the free energy of a rarefied gas comprising rigid rods is employed, and the Flory method,[125] based on the lattice model of the polymer. The present development of the Onsager theory has been described by Khokhlov and Semenov.[126]

Unfortunately, an analytical treatment can be rarely continued until numerical results are obtained, which applies particularly to the most interesting semirigid chains, for which $L$ is frequently comparable to $A$. The computer simulation of such systems is therefore evidently essential.

*Equilibrium properties.* The question of the conditions governing the transition to the liquid crystal state and the conformational changes in the orientational ordering of semirigid chains was first solved by the MC method.[127] Chains with free internal rotation, consisting of $N$ rigid units with a single diameter $\sigma$ connected by bonds of unit length at a specified angle $\alpha$, were considered. The angle $\alpha$ was chosen so that the local asymmetry parameter $A/\sigma$ was 57.7 and the criterial Flory parameter $f$ was 0.074, which reproduced the value of $f$ for the nitrocellulose chain.[13] The results of the calculation for 40-unit chains are presented in Fig.8, which illustrates the dependence of the quantity $\langle R^2 \rangle$ and the orientational order parameter $\eta = [(3 < \cos^2\gamma) - 1]/2$ ($\gamma$ is the angle between the vector R connecting the ends of the chain and the director of the specimen) on the number-average density $\rho$. Evidently, for low values of $\rho$, the parameter $\eta \cong 0$, i.e. the system is isotropic. Appreciable changes in $\eta$ and $\langle R^2 \rangle$ begin only at $\rho \geqslant 0.1$, where these quantities exhibit a rapid increase. The increase in $\eta$ shows that the system passes to a liquid crystal state (of the nematic type). The transition is accompanied by an increase in the length and rigidity of the chains. For $\rho \to 1$, it was found that $\langle R^2 \rangle \to L^2$. This effect constitutes a fundamental difference between the behaviour of semirigid and flexible chains. For comparison, Fig.8 illustrates the concentration variation of $\langle R^2 \rangle$ calculated for the same system of 40-unit chains but exhibiting a high flexibility ($\alpha = 90°$ and $A/\sigma = 1$). In this case the picture is completely reversed: with increase in $\rho$, the order parameter does not change and is close to zero, while $\langle R^2 \rangle$ tends to $\langle R_0^2 \rangle$. It has been shown[127] that the order effects, observed in the system of semirigid macromolecules, depend only slightly on the attractive forces. As for low-molecular-weight liquid crystal systems, the repulsive component of the interaction potential plays the main role.

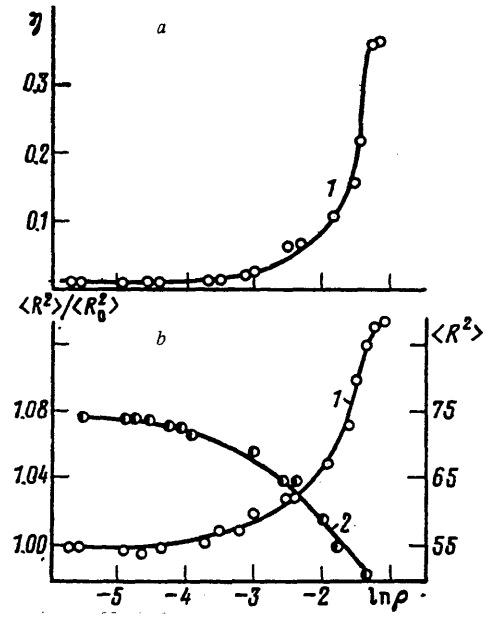



**Figure 8.** Dependence of the order parameter (*a*) and average chain dimensions (b) on the density: 1) system of semirigid chains (the quantity $\langle R^2 \rangle$ is expressed relative to the size of an isolated chain); 2) system of flexible chains.[127]

The results of the computer experiment[127] can be compared with theoretical predictions.[126] For the model considered by Pletneva et al.,[127] the ratio $L/A = 0.67$ and the critical density at the transition point $\rho_c$, estimated from the maximum in the derivative $d\eta/d\rho$, was found to be 0.23 (under these conditions, $\eta_c = 0.37$). The theory[126] yielded $\rho_c = 0.26$ and $\eta_c = 0.41$ for the same $L/A$ ratio. The agreement with the computer calculation is clearly extremely good. We may note that the Flory theory[125] yields a low critical density for the model investigated.[127]

The theoretical study[124,126] was based on the second virial approximation and its applicability is therefore restricted to the range of comparatively low polymer concentrations. On the other hand, the lattice model[125] describes the ordering in concentrated systems. Nevertheless, MC calculations[128] for the two-dimensional lattice model with $\rho = 0.952$ revealed significant deviations from the Flory theory. Recently the same workers[129] carried out an analogous calculation for a three-dimensional system of chains ($N = 20$) on a cubic lattice (441 chains with $\rho = 0.952$). The rigidity of the chain was regulated by the parameter $\Delta\epsilon$, which determines the extent to which the forward step on the lattice (the *trans*-isomer) is preferred to the sideways step (the *gauche*-isomer). Approximately $3.5 \times 10^9$ configurations were generated for each $\Delta\epsilon$ using the "quasi-reptation" algorithm.[60]

The results of the calculation of $\eta$ and of the average fraction of the *gauche*-bonds $p_G$ are presented in Fig. 9. These values can also be found within the framework of the lattice theory,[125] according to which the critical transition temperature $kT/\Delta\varepsilon_c = 0.56$ for $N = 20$ in the absence of unoccupied sites on the lattice. Calculation by the MC methods has shown that, with decrease of $kT/\Delta\varepsilon_c$ (i.e. with increase of the rigidity of the chains), there is a sharp transition at the point $kT/\Delta\varepsilon_c = 0.64$: the chains are almost completely uncoiled and ordered. Evidently, in the three-dimensional case there is a satisfactory correlation between the critical values of $kT/\Delta\varepsilon_c$ obtained theoretically[125] and in the computer experiment. On the other hand, the computer calculation reveals the phenomenon of hysteresis: the reverse transition from the ordered to the disordered states takes place at a different point $kT/\Delta\varepsilon'_c = 0.68$. The description of this behaviour is outside the framework of the theory.[125]

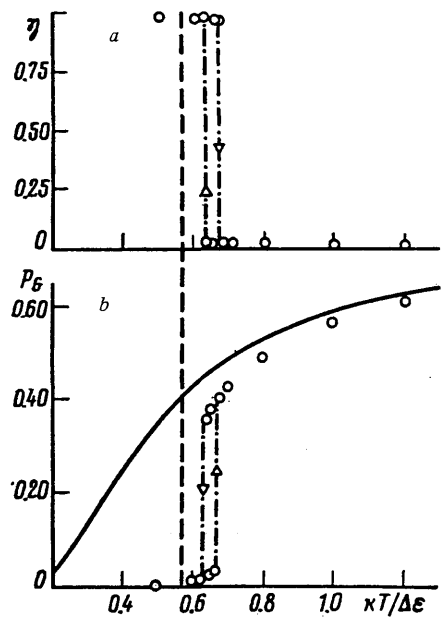



Figure 9. Dependence of the order parameters (*a*) and the average fraction of *gauche*-bonds (*b*) on the reduced temperature for the lattice model of a liquid crystal. Symbols—calculation by the Monte Carlo method (the arrows indicate the direction of the forward and reverse transitions); continuous curve—calculation based on the Flory theory; the dashed line indicates the critical transition temperature in the Flory theory.[125]

It must be emphasised that, in the examples described above, the rigid chains were ordered without any involvement of the attraction forces, solely as a result of packing effects. In a number of instances packing effects can cause the orientational ordering of flexible chain polymers. For this purpose, it is sufficient to restrict the mobility of the chains in space. Computer experiments have shown[130–132] that flexible chains "tied" by one end to an impermeable surface (for example, as a result of the strong adsorption of the terminal polar group or chemical "grafting") are capable of orientational ordering solely as a result of the steric hindrance, which depends on the degree of surface coverage. Another possibility for the transition of flexible chains to an ordered state is associated either with the presence of external orienting fields or with the anisotropy of the intermolecular interaction forces.[133]

*Dynamic properties.* There have been few studies on the modelling of partly ordered polymer systems by the MC method. Pershin and Skopinov[134] examined a two-dimensional system of rigid five-centre molecules and observed a tendency towards the formation of short-lived associated species (clusters) in which the degree of local order was higher than the average for the system. The association of molecules following their mutual approach is caused, according to the authors, by potential barriers preventing the shear displacement and stabilising a parallel configuration.

The dynamics of the behaviour of molecules having the form of infinitely rigid rods has been studied.[135] Although the cross-sectional area of the rods was assumed to be zero, they could not cross each other. Depending on the reduced density $\rho^* = NL^3/V$ (where $N$ is the number of rods with a length $L$ in a volume $V$), the AF for the rates of self-diffusion coefficients

$$D = (D_{\parallel} + 2 \cdot D_{\perp})/3,$$

where $D_{\parallel}$ and $D_{\perp}$ are diffusion coefficients in the longitudinal and transverse directions, were calculated. It was shown that, during the period between two collisions, the movement is free and not diffusional. For low values of $\rho^*$, the transport properties are described satisfactorily by the kinetic Enskog theory.[22] However, for $\rho^* \geqslant 8$, this treatment ceases to be valid. It was found for this range of densities that the rotational diffusion coefficient of the rod decreases as $(\rho^*)^{-2}$ or as $L^{-6}$, in conformity with the theory of Doi and Edwards.[136]

Table 2. The diffusion coefficient of rods and its longitudinal and transverse components for different reduced densities.[135]

| $\rho^*$ | $D$ | $D_{\parallel}$ | $D_{\perp}$ | $\rho^*$ | $D$ | $D_{\parallel}$ | $D_{\perp}$ |
|---|---|---|---|---|---|---|---|
| 1 | 2.40 | 2.59 | 2.30 | 16 | 0.24 | 0.50 | 0.11 |
| 2 | 1.16 | 1.37 | 1.05 | 24 | 0.21 | 0.49 | 0.073 |
| 4 | 0.61 | 0.82 | 0.51 | 32 | 0.20 | 0.50 | 0.049 |
| 6 | 0.44 | 0.60 | 0.36 | 40 | 0.23 | 0.64 | 0.031 |
| 8 | 0.34 | 0.53 | 0.25 | 48 | 0.34 | 0.97 | 0.025 |

In the study of translational motion, a fairly unexpected result was obtained. It was found that, in a sufficiently dense system, an increase of $\rho^*$ entails not a decrease of $D$ and $D_{\parallel}$, as seemingly should have been the case, but in fact their increase (Table 2). Such behaviour is associated with the fact that in a system of infinitely thin rods a change in the component of the velocity along the rod axis can occur only after a change in the rate of rotation as a result of the collision. However, for a high density and for long times, the maximum contribution to the corresponding component of the AF for the velocity $C(\mathbf{v}_{\parallel}, t)$ comes only from the rods for which the rotational component of the movement is minimal. Although the fraction of such particles in the

system may be small, nevertheless they play an increasingly significant role with increase in $\rho^*$. Therefore, the higher the value of $\rho^*$, the greater the extent to which $D$ and $D_\parallel$ are determined by particles with the maximum longitudinal velocity component.

### 2. The Effect of Orienting Fields

Luk'yanov et al.[137] investigated by the MD method the influence of the orienting field on flexible six-unit chains in a dense system. Each bond was acted upon by an orienting quadrupolar potential $U = -K\cos^2\gamma$, where $\gamma$ is the angle between the bond vector b and the direction of the field. It was shown that the degree of order in the system increases with increase in $K$ and that the order parameter $\eta$ is close to unity for $K \cong 10\ kT$.

Calculations of the orientation AF for the vectors b indicated an anisotropy of the relaxation properties, which is manifested in the different rates of decrease of the AF components: along the field ($C_\gamma$) and in the transverse direction ($C_\beta$). It was found that the corresponding characteristic times behave differently with increased $K$: $t_\gamma$ increases while $t_\beta$ falls. This is associated with the operation of two mechanisms of the orientational mobility: (1) rapid rotational-vibrational movements of b in the potential well generated by the field and (2) transitions across the potential barrier separating two equilibrium positions of b (parallel and antiparallel to the field). For the relaxation of $C_\gamma$, transitions precisely through this barrier are necessary, their frequency decreasing with increase of $K$. On the other hand, the relaxation of $C_\beta$ does not require that a barrier be overcome; vibrations at the bottom of the potential well are sufficient for this purpose and their frequency increases with increasing steepness of the potential.

The molecular dynamics of liquid alkanes has been studied in the field of external compressing and displacing forces.[138] Their intramolecular vibrational and rotational movements were considered and it was established that the external forces cause only a reorientation of the molecules but do not alter their distribution with respect to conformational states. The authors concluded that, in real experiments designed to study double refraction in a flow (the Maxwell dynamo-optical effect), the conformational composition of short hydrocarbon chains should not change appreciably compared with the static system in the absence of shear stresses.

The deformation of polyethylene chains stretched by pulling on the ends has been investigated by the MC method.[139] The "isoenergetic mechanism" of the increase in length, according to which the initial increase in length is due to a redistribution of the conformers in the chain and the change in the conformational composition begins only after numerous repetitions of the stretching process (~0.6), was confirmed.

### 3. The Rotational-Crystalline State

In a rotational crystal there is a possibility of the rotation of the molecules about their long axes, whereas the axes themselves retain an ordered arrangement. This state is characteristic of normal paraffins. Computer modelling of a rotational system has been carried out by the MD method.[140] A system comprising $C_{10}H_{22}$ molecules, in which the extreme H atoms were kept near the opposite ends of the chain (prism 1.3 nm high) by a harmonic potential, was considered. The chains bounding the cell along the $x$ and $y$ axes were stationary and 17 internal chains migrated in accordance with Newton's equations. The interaction of the C and H atoms was described by the atom–atom potentials. At the end of the initial relaxation period, numerical experiments

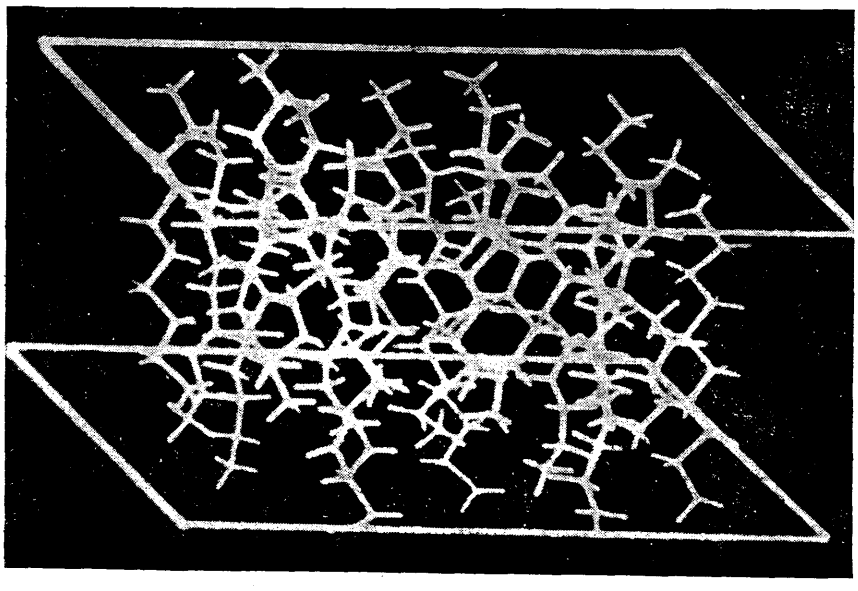


Figure 10. A film frame demonstrating the dynamics of the change in the configuration of a rotational hydrocarbon crystal.[40] The ends of the chains are held outside two opposite planes by a harmonic potential. The stationary chains bounding the cell are not shown; only the bonds between the C and H atoms are represented but not the atoms themselves.

were carried out at time intervals of ~7 ps (which corresponds to approximately three characteristic time units $\tau$). The calculation showed that the rotational-crystalline state, in which the internal paraffin chains in the cell rotate, obtains at temperatures in the range 205–269 K. At 205 K the amplitude of the torsional vibrations of the torsional C–C angles via the equilibrium position reaches 60°, while at 269 K it reaches 120°.

Balabaev et al.[140] filmed a graphical computer display on which the configurations of a rotational crystal were shown in succession. In a literal sense, the film makes it possible to see and analyse all the details of the movements of atoms in the system (Fig.10). Visualisation of information of this kind is a powerful means for a clear description of complex molecular models in the course of a dynamic computer experiment.

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The examples of the use of the computer experiment method examined in this review by no means exhaust the numerous problems which are solved with its aid in the chemistry and physics of polymers. One may mention in addition computer studies of chemical macromolecular reactions[141] and gel formation phenomena,[142,143] the structures and mechanical properties of polymer networks,[144,145] the mechanisms of the breakdown of solid polymers,[146] crystallisation kinetics,[147] and topological effects in polymers.[148,149] The first attempts have been made to model non-equilibrium systems[150,151] and complex macromolecular objects of biological origin, for example, biological membranes.[130–132,152–157] The computer experiment frequently constitutes the only source of unique information. Vigorous studies have been initiated recently on the mathematical modelling of biopolymers: polypeptides and globular proteins in the course of their functioning[10,11,158–183] and also polynucleotides.[184–189]

Further progress in the chemistry of simulation modelling of molecular systems is probably to be expected not so much in the development of the numerical methods themselves as in the solution of strictly engineering problems in the construction of multiprocessor special purpose computers. An ideal procedure for the study of a system of $N$ interacting particles would involve the use of a computing device having the same number of $N$ microprocessors working in parallel, each of which would carry out calculations for only one particle. Calculations on specialised computers of this kind have already been reported in the literature.[190,191] Considerable advances have been achieved using computers with a vector processor.[192,193] Definite hopes for a qualitative improvement of the effectiveness of the numerical modelling of many systems are nowadays associated also with the prospect for the creation of a computer on the basis of the so-called reversible cellular automatic device.[194,195]

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# The Specific Features of the Interaction of Ionising Radiation with a Molecular Medium and the Role of Tracks in Radiation Chemistry

I.G.Kaplan and A.M.Miterev

The interactions of charged particles with a molecular medium are surveyed and the highly excited molecular states arising under these conditions are discussed. The processes involving the absorption of energy in a condensed phase and the role of collective excitations are considered in detail. The relation between the structure of the track and the characteristics of the radiation-chemical reactions in the tracks of particles of different kinds is analysed.
The bibliography includes 170 references.

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## I. INTRODUCTION

When charged particles pass through a substance, their interaction with the atoms and molecules of the medium results in energy transfer to the medium. This energy is consumed mainly in the excitation and ionisation of the medium. The energy of slow, heavy particles is converted into the kinetic energy of the movement of the atoms of the medium. In solids, when the transmitted kinetic energy is sufficiently large, atoms can be dislodged from their equilibrium positions. As a result, regions with a damaged structure are formed in the irradiated medium in which molecular excited states, positive and negative ions, and secondary electrons dislodged from atoms and ions are localised. All these defects are concentrated along the trajectory of the primary particle and form a track in the given substance. Since the effect of hard electromagnetic radiation on matter involves the dislodgement of fast Compton electrons and photoelectrons, the tracks of X-rays and $\gamma$-rays reduce to the tracks of fast electrons distributed throughout the specimen.

The tracks of $\alpha$-particles and the electrons dislodged by X-rays were first observed visually in the Wilson cloud chamber. Subsequently bubble and spark chambers were developed. Detectors based on the determination of the change in the structure of the specimen by treating the latter with appropriate chemical reagents have come to be widely used for the detection of tracks. They include primarily photoemulsions and also different types of solid detectors.[1]

Experimental observations of tracks yield in the first place information about the charged particle itself (mass and charge) and play an important role in the identification

of unknown elementary particles. As regards the characteristics of the track of the particle, they make it possible to measure only the ionisation density in gases along the track and to find specific energy losses. However, such information is quite inadequate to explain the changes which occur in the molecular medium on passage of ionising radiation. The microstructure of the short-lived regions of primary excitations and ionisations along the particle track is of decisive importance for the final chemical reactions. In order to achieve agreement between the theoretical model of the radiolysis of water and experimental data, it was necessary to take into account the non-uniform distribution of the active intermediate species in the electron tracks.[2,3]

The spectrum of the states arising on exposure of the medium to ionising radiation is much more complex than in the case where the medium is irradiated with light. The former includes states in the region of the continuous spectrum corresponding to the ionisation of electrons from the inner shells of the molecules with subsequent cascade of ionisations owing to the "shake-up" and Auger effects, the collective states of the plasmon type, and the so-called "superexcited" states.[4] All these states are short-lived, decomposing after $10^{-16}$–$10^{-12}$ s into active intermediates which initiate the chain of radiation-chemical reactions.

Since the instantaneous picture of the primary distribution of excitations on ionisation cannot be measured directly, it is investigated by numerical experiment on a computer. The passage of ionising radiation through matter is modelled with the aid of the statistical test method (the Monte Carlo method). In order to model the passage of radiation, it is necessary to know the excitation and ionisation cross-sections of the molecules.

Computer modelling makes it possible to find the spatial and energy distribution of the dislodged electrons and the densities of the ions and excited states generated at different distances from the axis of the particle track. The spatial-energy structure of the tract is a characteristic of the radiation which contains much more information than the usually employed characteristic—the linear energy loss (LEL). Knowing the structure of the track, it is possible to identify the characteristics of the primary radiation-chemical reactions in the tracks of particles of different kinds.[5] The evolution of ideas about the role of tracks in radiation chemistry can be traced in the relevant reviews.[6,7]

In the present review we have endeavoured to deal with the entire set of questions associated with the primary stage of radiolysis and its influence on the subsequent chemical reactions. The consecutive pattern of the physicochemical processes arising in the medium on irradiation is examined: from the initial physical stage of the radiolysis, in the discussion of which much attention has been devoted to the specific features of the condensed phase which are not usually taken into account, to the subsequent physicochemical stage. Much space has been devoted to the discussion of the relation between the structure of the track and the character of the radiation-chemical reactions occurring in it.

## II. INTERACTIONS OF CHARGED PARTICLES WITH ATOMS AND MOLECULES

Since numerous books and reviews (see, for example, Refs. 8–13) have been devoted to the interactions of charged particles with an atomic-molecular medium, we shall confine ourselves in the present review to a brief discussion of the question and shall quote a series of formulae used in calculations of the degradation of the energy of the charged particles in the medium.

Fairly simple analytical expressions for the inelastic scattering cross-sections are valid in the case of fast particles, whose velocity is high compared with the velocities of atomic electrons [the energy of the particle $E \gg (M/m)E_b^a$, where M is the mass of the particle, $m$ the mass of the electron, and $E_b^a$ the binding energy of the electron in the atom]. For a sufficiently high transmitted energy $\varepsilon \gg I_n$ (where $I_n$ is the potential of ionisation from the $n$th electron shell), the dislodged electron can be regarded as free and the scattering cross-section is defined by the familiar Rutherford formula

$$d\sigma = (2\pi Z^2 e^4/mv^2\varepsilon^2)\,d\varepsilon, \qquad (1)$$

where $Z$ and $v$ are the charge and velocity of the arriving particle. Such collisions have come to be referred to as short-range or knockout collisions. For energy transfers leading to the excitation of an atom or molecule to the $n$th quantum state from the initial zero-point state with a transition energy $\hbar\omega_{0n}$ (such collisions are referred to as long-range or glancing collisions), the cross-section is estimated from the Bethe formula[9]

$$d\sigma_{0n}(q) = (4\pi Z^2 e^4 f_{0n}(q)/mv^2\hbar\omega_{0n}q)\,dq \qquad (2)$$

where $\hbar q$ is the absolute magnitude of the transmitted momentum and $f_{0n}(q)$ the generalised oscillator strength introduced by Bethe.[9] The generalised oscillator strengths as well as semiempirical formulae for the ionisation cross-sections and total non-elastic scattering cross-sections may be found in a series of publications.[12–17]

For polyatomic molecules, the ionisation cross-section can be represented by an additive quantity. For the $H_2O$ molecule, the experimental ionisation cross-sections in the electron energy range from 0.1 to 20 keV have been expressed[18] in the form $\sigma_i(H_2O) = \sigma_i(H_2) + \frac{1}{2}\sigma_i(O_2)$. The differences between such additive cross-sections and the experimental cross-sections are insignificant over the entire calculated range. It has been shown[19] that the ionisation cross-section of a molecule can be quite accurately represented by the sum of the ionisation cross-sections of the chemical bonds. Having analysed the experimental data for the ionisation cross-sections of 40 hydrocarbon molecules of different kinds, Grosse and Bothe[19] calculated the effective ionisation cross-sections of the C–H, $\pi$(C–C), $\sigma$(C–C), C–O, and other bonds. The values obtained make it possible to represent approximately the ionisation cross-section of an arbitrary molecule with the given chemical bonds to within 2%. Such additivity had been observed earlier in another study.[20]

In the investigation of the effect of charged particles on matter, it becomes necessary not only to estimate the cross-sections but also to find the probabilities of the excitation or ionisation of a species as a function of its distance from the axis of the track (the impact parameter) $\rho$. For this purpose, one uses a quasi-classical approach, according to which it is assumed that the charged particle moves along a definite trajectory, is structureless, and can be regarded as merely the source of a variable electromagnetic field. This approach is most legitimate for heavy charged particles.

The trajectory of a heavy charged particle in a substance is to a large extent linear, since, with the exception of the knock out collisions, the interaction with the atoms of the medium hardly causes a curvature in its path. For long-range collisions, one can find in this instance the dependence of the probability of the excitation of the $n$th quantum state of the atom (molecule) on the impact parameter $\rho$. The expansion of the Coulombic interaction operator into a multipolar series and the restriction of the latter to the dipolar term lead to the following expression for the probability of the transition of the system to the $n$th quantum state in terms

of the first-order perturbation theory:[21]

$$W_{0n}(\rho) = (Z^2e^4/\hbar^2)\left|\int_{-\infty}^{\infty} \frac{x_{0n}vt + y_{0n}\rho}{[(vt)^2+\rho^2]^{3/2}} \exp(i\omega_{0n}t)\,dt\right|^2, \quad (3)$$

where

$$x_{0n} = \sum_{i=1}^{N} \langle\psi_n|x_i|\psi_0\rangle; \quad y_{0n} = \sum_{i=1}^{N} \langle\psi_n|y_i|\psi_0\rangle, \quad (4)$$

$\psi_n$ and $\psi_0$ are the wave functions of the $N$-electron system, and the $x$ axis is directed along the trajectory of the incoming particle. The integrand decreases in inverse proportion to the cube of the distance from the axis of the tract and the interaction is therefore significant only in the region of distances of closest approach.

It can be shown that the effective collision is $\tau \cong 2\rho/v$. The collision is regarded as adiabatic if the collision time is much greater than the period of the quantum transition $2\pi/\omega_{0n}$, i.e. the inequality

$$\omega_{0n}\rho/\pi v \gg 1 \quad (5)$$

holds. In this case the integrand in Eqn.(3) oscillates repeatedly during the period of the collision and the integral is close to zero. Consequently atoms are not excited in an adiabatic collision.

The condition specified by inequality (5) is too strong: the "much greater than" sign should be replaced by the "greater than" sign, i.e. for excitation it is sufficient that the effective collision time should be less than the quantum transition time. To demonstrate this rigorously, it is necessary to calculate integral (3). After representing the exponential function in the integrand by a cosine and a sine using Euler's formula and integrating by parts, we obtain

$$W_{0n}(\rho) = \frac{4Z^2e^4\omega_{0n}^2}{\hbar^2v^4}[|x_{0n}|^2K_0^2(\eta) + |y_{0n}|^2K_1^2(\eta)] \quad (6)$$

where $\eta = \omega_{0n}\rho/v$ and $K_0(\eta)$ and $K_1(\eta)$ are modified Bessel functions (Macdonald functions[22]). For $\eta = \pi$, the functions $K_0^2(\eta)$ and $K_1^2(\eta)$ are almost zero (see the graph on p.196 of Ref.22). After setting $\eta = \pi$, we find the effective size of the region of direct excitations:

$$b_{\text{eff}} = \pi v/\omega_{0n}. \quad (7)$$

Thus the excitation has an appreciable probability for $\rho \leq b_{\text{eff}}$.

According to Eqn.(2), the excitation cross-section is proportional to the oscillator strength of the quantum transition. The latter is non-zero only for transitions without a change in the total electron spin. Since the ground state of the molecules is of the singlet type [only the $O_2$ ($S = 1$) and NO ($S = 1/2$) molecules are exceptions], a fast charged particle excites only singlet states on interaction with a molecule. As in irradiation by light, the triplet states are then populated via radiationless intersystem crossing transitions S → T.[23,24] Further, we may note that in the calculations of the cross-sections described above no account was taken of the terms due to electron exchange. When these terms are taken into account, the probability of the excitation of triplet states is not zero. The excitation cross-section for a triplet state has been shown[25] to be proportional to $E^{-3}$, i.e. it decreases very rapidly with increase of the electron energy (while the excitation cross-section for singlet states is proportional to $E^{-1}\ln E$). The excitation of triplet states is therefore effective only for low electron energies. Ochkur's formula[25] has been modified by Rudge[26] and calculations of the excitation of triplet states by the Ochkur–Rudge formula can be found in two communications.[27,28]

Molecules in triplet states exhibit an enhanced reactivity and are longer-lived and it is therefore important to estimate the relative probability of triplet excitations. One of the authors of this review showed[29] that, when a substance is irradiated by a stream of charged particles, at least two additional mechanisms for the population of triplet states appear compared with irradiation by light. In the first place, there is the generation of triplet states on recombination of a positive ion with a thermalised electron. As a consequence of the high statistical weight of the triplet state, the probability of the formation of a molecule in this state is three times greater than in the singlet state.[30] The second possibility arises because slow electrons with $E < 100$ eV, which effectively excite triplet states, predominate in the spectrum of secondary electrons. In this respect the most favourable conditions are created on irradiation with heavy ions, since, having as a rule low velocities, the latter generate low-energy secondary electrons. As a result, the role of triplet states in radiation-chemical processes should be much greater than in photochemistry.[29] Experimental evidence for this, based on the measurement of the relative phosphorescence and fluorescence yields, has been published.[31]

Any electron whose energy is less than the lowest electronic excitation level of the medium is referred to as a "subexcitation electron". It is not able to transfer its energy for the excitation of electrons, but its energy is sufficient to excite molecular vibrations and rotations. Furthermore, subexcitation electrons can lose energy in elastic collisions and also in processes involving their capture by a molecule or a positive ion. The behaviour of subexcitation electrons therefore depends on the process which predominates in the given medium (see Section VI below).

## III. THE NATURE OF THE HIGHLY EXCITED MOLECULAR STATES ARISING ON EXPOSURE TO IONISING RADIATION

In contrast to photochemistry, in radiation chemistry the energy of the radiation is so high that the transfer to molecules of energy greatly exceeding their ionisation potential becomes possible. This results in the formation of both discrete high-energy states in the autoionisation region of the spectrum (the so-called "superexcited" states—see below) and states in the region of continuous spectrum which arise owing to the ionisation of electrons in the inner shells of the molecule and are accompanied by the appearance of the corresponding vacancies ("holes"). An ion with a vacancy in an inner shell must be regarded as in a highly excited state with energy equal to the reorganisation energy of the electron shell of the molecule on formation of the vacancy. This energy can be either transmitted to one or several electrons of the molecule with a subsequent ionisation or transfer to unoccupied orbitals (the Auger effect[32–34]—see Fig.1) or can be radiated in the form of an X-ray quantum.

Repeated ionisation is characteristic of molecules consisting of light atoms on dislodgement of an electron from an inner shell, whereas fluorescence begins to be manifested appreciably only for elements with an atomic number $Z_a > 30$. The ratio of the probabilities of the Auger effect and X-ray fluorescence is $W_a/W_r \cong 10^6/Z_a^4$.[32] Table 1 lists the probabilities $W_a$ and $W_r$, the width of the levels $\Delta E$, and the yields of the fluorescence associated with the $K$–$LL$ transition for a series of atoms. For light elements (and also for their chemical compounds), the probability of emission is very low, while for heavy elements the opposite behaviour is observed. Thus the $K$-fluorescence yield is 0.96 for thallium ($Z_a = 81$).[32]

Although processes involving the dislodgement of an electron from inner shells take place much more rarely than those where an electron is dislodged from outer shells (the degradation spectrum is displaced towards low-energy electrons), their role is very important owing to the high probability of the subsequent repeated ionisation. The yield of ionisation from the $K$ shells of light elements has been estimated[35] as $g_K \cong 10^{-2}$ per 100 eV of the absorbed energy, i.e. the absorption by the medium of an electron having an energy of 1 MeV results in the formation of approximately $10^2$ ions with a hole in the $K$ shell. For comparison, we may point out that the average number of ions formed under these conditions is approximately $3 \times 10^4$, since approximately 30 eV is consumed in the formation of a pair of ions. However, the abstraction of a $K$ electron causes a cascade of subsequent ionisations.

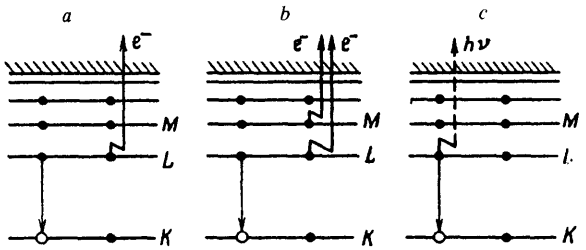



**Figure 1.** The possible forms of the evolution of the state with a vacancy in the $K$ shell: *a*) $KLL$–Auger effect; *b*) double $KLIM$–Auger effect; c) emission of the $K_\alpha$ X-ray line. In processes *a* and *b* the electron can pass to an unoccupied orbital instead of undergoing a transition to the continuous spectrum.

**Table 1.** The probabilities of the radiative and Auger–$KLL$ transitions for different atoms.[32]

| Atom | $Z_a$ | $10^{-14} W_a$, $s^{-1}$ | $10^{-14} W_r$, $s^{-1}$ | $\Delta E$, eV | $W_r/(W_a+W_r)$ |
|---|---|---|---|---|---|
| Ne | 10 | 7.40 | 0.063 | 0.98 | 0.0085 |
| Mg | 12 | 8.07 | 0.130 | 1.07 | 0.016 |
| Ar | 18 | 11.29 | 0.83 | 1.59 | 0.068 |
| Ni | 28 | 12.23 | 4.85 | 2.24 | 0.284 |
| Kr | 36 | 13.46 | 14.39 | 3.65 | 0.517 |

There are two physical mechanisms leading to ionisation on formation of a vacancy in an inner electron shell. One of these is due to the "shake-up" of the electron shell on dislodgement of an inner electron. On dislodgement of an inner electron the sharp change in the electromagnetic field in which the outer electrons move leads to additional ionisation (for a more detailed description of the "shake-up" mechanism, see the review of Matveev and Parilis[33]). The other mechanism is due to the Auger effect,[32] where an electron is transferred from one of the higher orbitals to an unoccupied inner orbital and the energy evolved is transferred to one or several outer electrons (see Figs. 1*a* and 1c). This process can be regarded as internal conversion of the quantum of electromagnetic radiation emitted on transition of an electron from an upper to a lower level. The Auger effect occurs after the formation of a vacancy over a period of $10^{-15}$–$10^{-11}$ s (depending on the extent to which the transitions are allowed), while the "shake-up" of the electron shell accompanies the formation of a vacancy and takes place over a period of $10^{-16}$–$10^{-15}$ s. Both mechanisms contribute to the formation of multicharged ions.

**Table 2.** The relative yields of ions with different numbers of charges on irradiation of neon with X-rays.[36]

| Ion | $Ne^+$ | $Ne^{2+}$ | $Ne^{3+}$ | $Ne^{4+}$ | $Ne^{5+}$ |
|---|---|---|---|---|---|
| Yield, % | 6.5±0.7 | 68.5±2.0 | 22±2 | 2.8±0.5 | 0.3 |

The probability of repeated ionisation on dislodgement of an electron from the $K$ shell is very high. For example, it is almost 99% for neon ($Z_a = 10$). When an $L$ electron is dislodged, the probability of ionisation diminishes to 13%.[36] Table 2 lists the relative yields of Ne ions with different numbers of charges on irradiation of the gas with X-rays ($K_\alpha$ Al line with $E = 1256$ eV). The overall yield of multicharged ions is 93.5% (its value less than 99% is due to the ionisation from $L$ and higher shells). A similar distribution is to be expected also for light molecules. For heavier elements, the probability of the formation of ions with the number of charges $n \geq 4$ becomes greater than for doubly charged ions.[37]

The repeated ionisation of molecules on dislodgement of electrons from inner shells can lead to their decomposition into several positively charged fragments and can ultimately give rise to a sequence of reactions different from that in photochemistry. According to estimates,[38] this effect should increase in the ultra-relativistic range of energies of the incoming particles. It is also noteworthy that, among states with an internal vacancy, highly excited states of an ion, which are not populated on irradiation with light, are in fact populated (for example, there is a possibility of the formation of $N_2^+$ in the $C^2\Sigma^+$ state[39]).

The excitation of atoms to discrete states with energies higher than the first ionisation potential $I_1$ generally leads to autoionisation, which can be explained by the fact that in the case of atoms autoionisation takes place over a period of $10^{-14}$–$10^{-11}$ s, while the duration of emission, which is the only competing process, is $10^{-9}$–$10^{-6}$ s. Emission from autoionisation states takes place only in rare instances. Thus the autoionisation peaks for the O atom at $\lambda = 878$–$879$ and 791–793 Å are characterised by an ionisation efficiency $\eta(E) < 1$. Prohibitions owing to selection rules lead to lifespans of these states $\tau = 10^{-8}$ s, which makes possible their radiative decay.[40] For atoms, this is exceptional, but the situation is different for molecules.

Platzman[4] drew attention to the fact that, according to experiments on the irradiation of molecular gases by vacuum ultraviolet light, the probability of the ionisation of certain gases $\eta(E) < 1$ when $E > I_1$ (for $E$ exceeding $I_1$ by 10 eV and more). These results were confirmed by experiments[41] on mixtures incorporating a noble gas and various molecules. An isotope effect is then observed. The replacement of hydrogen by deuterium led to an increased probability of

ionisation. Hence Platzman concluded that there is an effective competition between autoionisation and predissociation. Platzman used the term "superexcited states" for discrete states with $E > I_1$ in which predissociation takes place (see the relevant reviews[7,42]). Subsequently we shall use the abbreviation SES for such states.

As a consequence of vibronic interactions, there is a possibility of yet another non-ionisation channel leading to the decomposition of SES—radiationless relaxation via the conversion of the electronic energy into the vibrational energy of molecules and, in the case of a condensed phase, into the thermal energy of the medium. For fluorescent molecules, there is a possibility of fluorescence from the lowest excited state (in conformity with Kasha's empirical rule,[43] the molecular fluorescence originates from the lowest excited level regardless of the wavelength of the exciting light).

The SES formation and decomposition reactions can be represented schematically as follows:

$$\mathrm{ABC} \xrightarrow{h\nu > I_1} \begin{cases} \longrightarrow \mathrm{ABC^+} + \mathrm{e^-} & \text{(direct ionisation);} \quad (8a) \\ \longrightarrow \mathrm{ABC^{**}} & \text{(formation of SES);} \quad (8b) \end{cases}$$

$$\mathrm{ABC^{**}} \begin{cases} \longrightarrow \mathrm{ABC^+} + \mathrm{e^-} & \text{(autoionisation);} \quad (9a) \\ \longrightarrow \mathrm{AB^*} + \mathrm{C^*} & \text{(predissociation);} \quad (9b) \\ \longrightarrow \mathrm{ABC} + \Delta E'_{vib} + h\nu_1 & \text{(radiative relaxation);} \quad (9c) \\ \longrightarrow \mathrm{ABC} + \Delta E_{vib} & \text{(radiationless relaxation).} \quad (9d) \end{cases}$$

In the optical approximation for small molecules, the radiation yield of SES is estimated as being within the limits $g_{SES} \cong 0.6$–$1$.[44] Analogous estimates have been made also by Bednar.[35]

The important role of SES in radiation chemistry consists in the fact that their decomposition involves the formation of highly excited products (radicals). Such "hot" radicals can enter into endothermic reactions. In his first fundamental study, Platzman[4] already pointed out the possibility of a reaction with direct formation of the molecular product:

$$\mathrm{H^* + H_2O \rightarrow H_2 + OH.} \quad (10)$$

A series of data indicate that molecular hydrogen is formed by an analogous pathway in the radiolysis of hydrocarbons.[42]

Three possible pathways leading to the formation of SES can be considered: (1) the excitation of an electron in an inner shell to an unoccupied orbital; (2) the formation of a Rydberg state, these are a sequence of hydrogen-like levels converging to the ionisation potential $I \geq I_1$; (3) excitation of two valance electrons.

Owing to their short lifespan, the states of the first type decompose via the Auger mechanism and cannot be classified as SES, since the latter are neutral. Hydrogen-like excited states, referred to as the Rydberg states, are much longer-lived. At any rate, this is the case when $I$ is not very large, i.e. a hole is formed in the valence shell (although deeper valence levels can also be involved). The interaction of the electronic and vibrational movements leads to predissociation. In the Rydberg state the electron is sufficiently remote from the positive ion and moves more slowly, which ensures the exchange of the electronic and vibrational energies.

A special case of SES consists of highly excited vibrational Rydberg states converging to $I_1$. The vibrational quanta added to the electronic energy (which is less than the ionisation potential) cause the transition of the electron to the state with $E > I_1$. Most of the autoionisation thresholds for $E$ which exceed $I_1$ by several electron-volts, have a vibronic, Rydberg origin.[40] In these states predissociation competes with autoionisation as a result of which $\eta(E)$ becomes less than unity. Such a possibility of the appearance of SES was first pointed out in a review by one of the present authors[7] and also by Nishikawa and Watanabe.[45] The role of Rydberg states in radiation chemistry has been discussed in two communications.[46,47]

The energy levels of the Rydberg states are described by the "hydrogen-like" formula

$$E_n = e^2/2a_0(n-\delta_R)^2, \quad (11)$$

where $n$ is the principal quantum number, $\delta_R$ the Rydberg shift of the level, and $a_0$ the Bohr radius. Eqn.(11) is valid for molecules for low values of $n$, when the distance between the electronic levels greatly exceeds the distance between the rotational and vibrational levels. With increase of $n$, the adiabatic approximation ceases to be valid. The interaction of the Rydberg electronic states with the rotational-vibrational movement leads to a marked broadening of the lines and the Rydberg spectrum becomes almost continuous. As a result, the lifespans of the molecular Rydberg states are smaller by many orders of magnitude than those of the atomic states. Thus the width of the Rydberg level in the $H_2$ molecule is 1–5 $cm^{-1}$ for autoionisation, where $n = 8$–$11$,[48] which corresponds to $\tau = \hbar/\Delta E \cong 10^{-12}$ s, i.e. is of the order of magnitude of the vibrational period.

The lifespan of the Rydberg states increases significantly when they are characterised by a large angular momentum $l$. Fano[49] showed that, when the energy of the incoming electron exceeds by several electron-volts the ionisation potential, then the formation and subsequent decomposition of the intermediate negative complex can result in the appearance of Rydberg states with a high orbital momentum $l$.[50] Owing to the appearance of a centrifugal barrier, the lifespan of such states increases greatly both relative to the autoionisation and predissociation states and relative to the radiative transition times. Evidently the nature of the Rydberg states where $\tau = 10^{-5}$–$10^{-4}$ s, which had been observed[51,52] for $N_2$, $O_2$, $CO_2$, $NH_3$, etc., is apparently the same. It must be emphasised that these long lifetimes have been recorded in a rarefied gas, while in a condensed phase the situation may be different.

The interaction of Rydberg levels with the vibrational-rotation motion in diatomic molecules has been investigated by Golubkov and Ivanov.[53] Rydberg states with a hole in an inner shell have not so far been considered theoretically. The behaviour of Rydberg states in a condensed phase likewise still remains virtually uninvestigated. In this case the demoninator in Eqn.(11) for the energy should include the dielectric constant of the medium $\varepsilon(\omega)$, since the radius of the Rydberg state can reach hundreds of Ångstroms and for this reason there may be numerous molecules between the positive ionic residue and the electron. It is still not clear to what extent the lifespan of the Rydberg states would decrease under these conditions.

The measurement of the intensity of the luminescence of the decomposition products as a function of the energy of the ionising radiation is an effective method for the identification of SES. A series of such measurements have been made.[54,55] Thus, after irradiating hydrocarbons with electrons, it has been shown that, when $E > I_1$, lines of the Balmer series for the H atoms appear, i.e. H* is formed. For $CH_4$, the threshold corresponding to the appearance of the Balmer lines is 21.8 eV, which greatly exceeds the ionisation potential $I_1 = 12.51$ eV. The intensity of the lines then diminishes consistently with increasing number of the lines $n$, which indicates the Rydberg nature of the SES formed on excitation of the inner valence electrons from non-bonding orbitals.

Experimental data demonstrating unambiguously the formation of SES on two-electron excitation have been published.[55] Measurements of the probabilities of the absorption of energy and ionisation showed that $\eta(E) < 1$ is observed for $CH_4$ in the range of energies from 27 to 80 eV. Since the highest ionisation potential of the valence electrons is 21.3 eV and the next potential corresponds to the ionisation of the K shell and is in the region of 290 eV, the formation of SES in the given instance corresponds to the excitation of two or more electrons.

Thus, among the three possible pathways dealing with the formation of SES the last two are actually realised.

## IV. ENERGY LOSSES OF A CHARGED PARTICLES IN A CONDENSED MEDIUM. COLLECTIVE STATES.

### 1. Ionisation Energy Losses by a Charged Species

Over most of the path traversed by fast charged species, the energy losses in the excitation and ionisation of the electrons of the medium make the main contribution to the retardation of such a species; these energy losses have come to be referred to as ionisation losses. Numerous publications have been devoted to the determination of the ionisation losses (see, for example, the relevant monographs[8-10, 56-58]). Among the various methods for the calculation of ionisation losses, the commonest is the Bethe–Bloch method, according to which the medium is considered to be an *ensemble* of independent atoms (molecules). The average ionisation losses per unit length of the path traversed were formulated thus:

$$S_e = -(\mathrm{d}E/\mathrm{d}x)_e = n_0 \sum_n \hbar\omega_{0n}\sigma_{0n}, \qquad (12)$$

where $n_0$ is the density of the species constituting the medium and the summation includes integration with respect to continuous states. Using for $\sigma_{0n}$ the formulae obtained within the framework of the Bethe theory for $S_e$, it is possible to obtain the following expression ($v/c \ll 1$) [10]

$$S_e = (4\pi Z^2 e^4 n_0 Z_a/mv^2) \ln (2mv^2/\bar{I}_a), \qquad (13)$$

where $\bar{I}_a$ denotes the average excitation potential of the atoms of the medium, introduced in accordance with the relation

$$Z_a \ln \bar{I}_a = \sum_n f_{0n} \ln (\hbar\omega_{0n}). \qquad (14)$$

The quantity $\bar{I}_a$ is best determined experimentally, although methods have been developed for its calculation (see the relevant review[59]). Formulae for $S_e$ taking into account the relativistic effects have been published.[8,56]

For molecular media and high energies of the charged species, the values of $S_e$ can be calculated according to the Bragg rule by means of an additive scheme. $Z_a$ and $\bar{I}_a$ in Eqns.(13) and (14) are then replaced by $N_m$ and $\bar{I}_m$ in conformity with the expressions

$$N_m = \sum_a n_a Z_a; \quad N_m \ln \bar{I}_m = \sum_a n_a \ln \bar{I}_a, \qquad (15)$$

where $n_a$ is the number of atoms of type $a$ in the molecule.

For velocities of the charged particles slightly exceeding the velocities of the valence electrons, the Bragg rule does not hold. For protons, appreciable discrepancies appear already for energies below 150 keV.[60] In calculations of $S_e$ in such cases, it is essential to introduce corrections for the effect of the binding of electrons (for details, see Starodubtsev[56] and Ahlen[59]).

In a condensed medium, for high velocities of the charged particles, the excitation condition (7) is fulfilled when the impact parameter $\rho$ has values significantly exceeding the average distance between the molecules. As a consequence of the polarisation of the medium by the moving charged particle, the interaction of the latter with distant molecules is weakened. As a result, the real energy losses become smaller than the values calculated by Eqn.(13) as the simple sum of the energy losses in individual collision steps.

One way of taking into account the influence of the macroscopic properties of the medium on the retardation of the charged particles is to introduce the dielectric constant of the medium $\varepsilon(\omega)$ into the differential cross-section for the inelastic interaction.[14,61] In the general case the linear response of the system to the electric field of the charge is defined in terms of the dielectric constant, which depends on the frequency and the wave vector $\varepsilon(\mathbf{q}, \omega)$. The quantity $\varepsilon(\mathbf{q}, \omega)$ is an extension (to fields which vary in space) of the dynamic dielectric constant $\varepsilon(\omega)$. The probability, referred to unit time, of the transfer of the momentum $\mathbf{q}$ and the energy $\hbar\omega$ (in terms of the Born approximation) from the charged particle to the electrons of the system is defined by the imaginary component of the reciprocal of the dielectric constant:[62]

$$W(q, \omega) = \frac{8\pi Z^2 e^2}{\hbar q^2} \operatorname{Im}\left[\frac{1}{\varepsilon(q, \omega)}\right] = \frac{8\pi Z^2 e^2}{\hbar q^2} \cdot \frac{\varepsilon_2(q, \omega)}{\varepsilon_1^2(q, \omega) + \varepsilon_2^2(q, \omega)}, \qquad (16)$$

where $\varepsilon_1(\mathbf{q}, \omega)$ and $\varepsilon_2(\mathbf{q}, \omega)$ are the real and imaginary components of the dielectric constant.

Eqn.(16) is used as the initial expression in the macroscopic consideration of the energy losses by the particle in its interaction with the electron gas. In recent years this expression has come to be used also for the calculation of the energy losses in molecular liquids (particularly in water[63]). However, the calculation of the energy losses by Eqn.(16) is extremely difficult because the explicit form of the function $\varepsilon(\mathbf{q}, \omega)$ is as a rule unknown (the electron gas is an exception).

### 2. Excitation of Collective States of the Plasmon Type in a Molecular Medium

In the condensed phase, broad, intense maxima in the range 15–25 eV appear in the energy loss spectra of fast electrons apart from the absorption maxima and energies close to the electronic transition energies in isolated molecules (Fig.2). These maxima have come to be referred to as the excitation of collective states of the plasmon type. The plasmon states are delocalised, i.e. they characterise the states of the entire assembly and not of individual molecules and their lifespan is short.

A theory of plasmon states has been devised by Bohm and Pines for free electrons in metals[64] and is fully consistent with experimental data for inelastic energy losses by fast electrons in metallic films. Although the possibility of collective excitations of the plasmon type in molecular media was pointed out by Fano as early as 1960,[65] this question remained controversial for a long time (see the relevant discussion in a number of communications[7,47,66]). In 1974 Brandt and Ritchie (quoted by Kutcher and Green[66]) formulated the criteria which must be satisfied by the dielectric function of the medium in the vicinity of the plasmon absorption point, while Heller et al.[67] showed that the criteria of Brandt and Ritchie are satisfied for a broad absorption peak in water with a maximum at 21.4 eV. Subsequently absorptions of the plasmon type were observed also in other molecular liquids[68] and in solid films.[83]

We shall deal briefly with the nature of the plasmon vibrations. Plasmons are defined as the quanta associated with the vibrations of the electron density of plasma. They can be regarded as coherent periodic deviations of the electron density at each point from its average value:

$$\Delta n(\mathbf{r}, t) = n(\mathbf{r}, t) - \bar{n} = \Delta n_{max} \exp[i(\omega t - \mathbf{qr})].$$

These vibrations are longitudinal, i.e. the direction of their propagation **q** coincides with the electric field strength vector **E**.

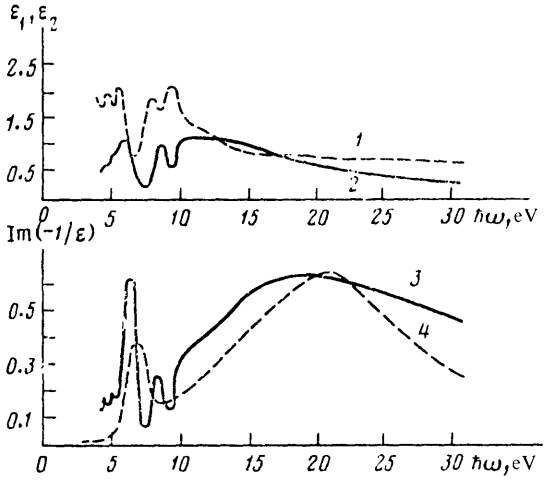



**Figure 2.** The form of the dielectric constant functions $\varepsilon_1(\omega)$ (curve *1*) and $\varepsilon_2(\omega)$ (curve *2*) and the energy loss function $\mathrm{Im}[-1/\varepsilon(\omega)]$ (curves *3* and *4*) in polystyrene; curve *3*—calculation based on $\varepsilon_1$ and $\varepsilon_2$ (Voltz[61]); curve *4*—experimental spectrum of the energy losses by electrons.[82]

According to Maxwell's equations, in the medium we have[61]

$$\mathrm{rot}\,\mathbf{H} = \frac{1}{c}\frac{\partial \mathbf{D}}{\partial t} + \frac{4\pi}{c}\mathbf{j} = i\omega\varepsilon(\omega)\mathbf{E} = 0. \qquad (17)$$

The magnetic field **H** = 0, since fields arising from the time variation of the electric induction vector **D** and the current **j** cancel out. An equation for the intrinsic frequencies of the plasmon vibrations follows from Eqn.(17):

$$\varepsilon(\omega) = 0. \qquad (18)$$

In the case of bound electrons, for example, in a molecular medium, the collective vibrations are not manifested in a pure form, being always combined with intramolecular transitions. The electron density vibrations can be represented in this case as a longitudinal polarisation wave, which leads to the vibrations of the dipole moment of the molecule. Such a wave is illustrated schematically in Fig.3 for non-polar molecules.

The passage of a fast particle with a velocity $v$ and a charge $e$ through the medium is equivalent to the current $\mathbf{j} = e\mathbf{v}\delta(x - vt)$. This entails the polarisation of the medium. The electric field $\mathbf{E}_{pol}$ arising as a result of this polarisation interacts with the moving particle, as a consequence of which the latter loses energy. By solving the Maxwell equations in the given medium, it is possible to find $\mathbf{E}_{pol}$ and to obtain an expression for the probability of the energy loss $\hbar\omega$ along the path of length $l$ for a single scattering of the particle in the solid angle $d^2\Omega$ owing to a deviation by an angle $\theta$:[69]

$$\frac{\partial^2 W}{\partial(\hbar\omega)\partial^2\Omega} = \frac{l}{(e\pi a_0 q)^2}\,\mathrm{Im}\left[-\frac{1}{\varepsilon(\mathbf{q}, \omega)}\right] \qquad (19)$$

where the momentum $q$ transmitted to the medium depends on the scattering angle and can be found from the laws of the conservation of the energy and momentum of the particle.

As in Eqn.(16), the principal dependence on the transmitted energy in Eqn.(19) consists in the factor $\mathrm{Im}[-1/\varepsilon(\mathbf{q}, \omega)]$. The maxima in the losses occur both in the region of the maxima in $\varepsilon_2(\mathbf{q}, \omega)$, which corresponds to allowed transitions in isolated molecules, and in the region of the zero values of the denominator, i.e. in the region corresponding to the solutions of Eqn.(18), which denotes the excitation of collective states; in order to find the frequencies, it is necessary to know the explicit form of the function $\varepsilon(\omega)$.

The medium with bound electrons can be represented by a set of oscillators, each of which is characterised by three parameters: the intrinsic frequency of the oscillator $\omega_i$, the oscillator strength $f_i$, and the decay constant $\gamma_i$ (a quantity which is equal to the reciprocal of the lifespan of the state). The following expression is valid for the dielectric constant of the medium in terms of the approximation $q \to 0$:[61,70]

$$\varepsilon(\omega) = 1 + \sum_i f_i\omega_p^2(\omega_i^2 - \omega^2 - i\gamma_i\omega)^{-1} \qquad (20)$$

where $\omega_p$ is the frequency of the plasma vibrations in the free electron system, which depends on the electron density $n_e$:

$$\omega_p = (4\pi n_e e^2/m)^{1/2}. \qquad (21)$$

Since the region $\hbar\omega < 30$ eV is important for the collective vibrations, the electrons in the inner atomic shells can be disregarded. The quantity $n_e$ is therefore determined by the density of the valence electrons and in the summation with respect to $i$ in Eqn.(20) it is necessary to consider oscillators corresponding to the transitions of valence electrons alone. An approximate expression for the frequency $\omega_p$ in molecular liquids has been published:[68]

$$\hbar\omega_p,\ \mathrm{eV} = 28.8\,(N_v\rho/M)^{1/2} \qquad (22)$$

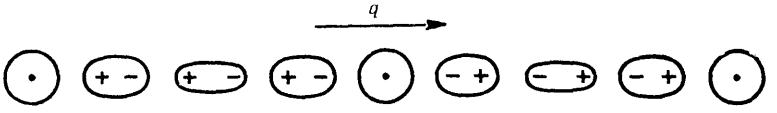



**Figure 3.** Schematic representation of the longitudinal polarisation wave in a condensed medium consisting of non-polar molecules.

where $N_v$ is the number of valence electrons per molecule, $M$ the molecular weight, and $\rho$ the density of the medium (g cm$^{-3}$); for water, $\hbar\omega_p \cong 19.2$ eV.

The intrinsic frequencies of the vibrations of the medium must satisfy Eqn.(18). It is very difficult to calculate these frequencies from Eqn.(20). We shall consider several special cases.

For free electrons in a metal, $f_0 = 1$, $\omega_0 = 0$, and all the $f_i = 0$ ($i \neq 0$);

$$\varepsilon(\omega) = 1 - \omega_p^2(\omega^2 - i\gamma_0\omega)^{-1}. \quad (23)$$

If the decay is slight, resonance is manifested at $\omega_2 = \omega_p$, i.e. free plasmons are excited.

In many molecules the maximum oscillator strength corresponds to one of the transitions. Suppose that it is $f_1$; in this case, one can put approximately

$$\varepsilon(\omega) = 1 + f_1\omega_p^2(\omega_1^2 - \omega^2 - i\gamma_1\omega)^{-1}. \quad (24)$$

For a weak decay, the energy loss function has only one maximum corresponding to $\varepsilon(\omega) = 0$:

$$\omega_r = (f_1\omega_p^2 + \omega_1^2)^{1/2}. \quad (25)$$

For low densities (gas phase), $\omega_p = 0$ and the maximum of the absorption function corresponds to $\omega_r = \omega_1$, i.e. as for an isolated molecule. In the opposite case, at very high densities, subject to the condition

$$f_1\omega_p^2 \gg \omega_1^2, \quad (26)$$

the quantity $\mathrm{Im}[-1/\varepsilon(\omega)]$ is a maximum for $\omega_r = f_1^{1/2}\omega_p$, i.e. corresponds to the longitudinal collective vibrations of free electrons. Peaks of the energy loss function between these two limiting cases cannot be fully assigned either to collective vibrations or to one-electron transitions. The latter situation is typical for molecular liquids.

The value of $\varepsilon_1(\omega)$, $\varepsilon_2(\omega)$, and the function $\mathrm{Im}[-1/\varepsilon(\omega)]$ in liquid water are presented in Fig.4. The $\varepsilon_2(\omega)$ peaks on the graph correspond to intramolecular transitions. The $\hbar\omega_1 = 13.5$ eV transition has the maximum oscillator strength $f_1 = 0.43$. The peak of the energy loss function $\mathrm{Im}[-1/\varepsilon(\omega)]$ at 21 eV is of plasmon origin, i.e. it corresponds to the longitudinal vibrations of the assembly of molecules. However, these are not the plasma vibrations of free electrons, since condition (26) is not explicitly fulfilled in this instance. Indeed, according to Eqn.(22), $\hbar\omega_p \cong 19.2$ eV for water. For the $\hbar\omega_1 = 13.5$ eV peak with $f_1 = 0.43$, we obtain $f_1(\hbar\omega_p)^2 = 159$ eV$^2$, while $(\hbar\omega_1)^2 = 182$ eV$^2$. Nevertheless, an appreciable change in the positions of the maximum indicates a relatively high contribution of the collective effects.

The theoretical determination of the energy loss function $\mathrm{Im}[-1/\varepsilon(\mathbf{q}, \omega)]$ is very difficult. In the region $q \to 0$ one can use optical data. For the electron gas, the expression for the dielectric constant has been obtained by Lindhard.[64] A semiempirical expression defining $\varepsilon(q, \omega)$ for water has been proposed.[71]

There are several ways in which collective excitations can break down. In the electron gas the breakdown takes place as a consequence of the interaction of the electrons with one another. The Coulombic interaction of electrons is strongly shielded by the electron cloud and is manifested only over short distances. As a result of such short-range interaction, the vibration energy of the plasmon is converted into the kinetic energy of the movement of individual electrons, i.e. it is distributed over the entire electron gas.[72]

In atomic-molecular media, the decay of plasmon states is due to the interaction of plasmons with electrons and also with the lattice vibrations or with impurities. The electron–plasmon interaction is of the long-range type. When a plasmon is absorbed, the momentum $\mathbf{q}$ is transferred to the electron; as a result, the collective excitation is converted into a one-particle excitation. This process is identical with the absorption of a photon having the same energy. Wölff[73] (see also Nazierea and Pines[74]) showed that the lifespan of the plasmon can be expressed in this case in terms of optical constants: the absorption coefficient $\kappa$ and the refractive index $n$:

$$1/\tau = n\kappa\omega. \quad (27)$$

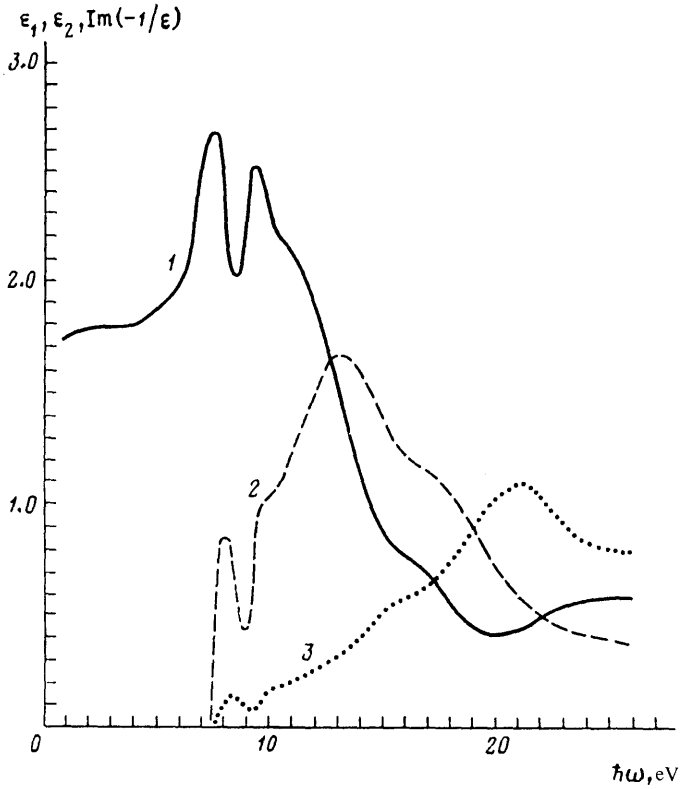



**Figure 4.** The form of the dielectric constant functions $\varepsilon_1(\omega)$ (curve *1*) and $\varepsilon_2(\omega)$ (curve *2*) and the energy loss function $\mathrm{Im}[-1/\varepsilon(\omega)]$ (curve *3*) in liquid water.[67]

For water in the region of the energy of the plasmon state, $\hbar\omega_r = 21.4$ eV, $n = 0.76$, and $\kappa = 0.36$.[67] Calculation by Eqn.(27) leads to $\tau \cong 1.1 \times 10^{-16}$ s. The lifespan of the plasmon state can be estimated also from the uncertainty relation. It follows from the spectrum of the energy losses in water that the half-width of the excited level with the energy $\hbar\omega_r = 21.4$ eV is $\Delta\hbar\omega_r/2 \cong 3.4$ eV. We therefore obtain $\tau = 1/\Delta\omega_r \cong 10^{-16}$ s, which agrees well with the calculation by Eqn.(27).

## V. THE LOCALISATION AND DELOCALISATION OF ENERGY LOSSES

The question of the degree of localisation of the absorbed energy arises from the study of the processes involving the absorption of the energy of the ionising radiation. There

are two possible causes of the delocalisation of its energy. The first is associated with the quantum-mechanical nature of the microparticle and the second with the possibility of collective excitations. We shall consider both causes in greater detail.

The quantum-mechanical nature of micro-objects is reflected by the uncertainty principle. The limitations imposed by the uncertainty principle were not previously taken into account in the study of the interaction of a stream of particles with matter. This was justified[75] by the fact that, during a period of $10^{-16}$ s, there is sufficient time for the localisation of the excitation as regards the molecules. However, this justification cannot be regarded as correct. It has been emphasised[47] that, since the subsequent localisation is stochastic, the initial delocalisation precludes in principle the determination of the site of the absorption of energy more precisely than is allowed by the uncertainty principle.

If a microparticle with the energy $E$ transmits the energy $\Delta E$ to the medium, then at the instant of the transfer the energy of the particle is defined to within $\Delta E$. This uncertainty $\Delta E$ in the energy is associated with the uncertainty $\Delta x$ in the position of the particle during the energy transfer process. This type of relation has been found for ultrarelativistic[75] and non-relativistic[47] particles. It has been shown[76] that in the general case the uncertainty as regards the coordinates of the particle during the transfer of its energy $\Delta E$ satisfies the inequality

$$\Delta x \geqslant \hbar v_x/\Delta E. \qquad (28)$$

The uncertainty in the site of the absorption of energy is the same.

The greater the energy transferred, the lower the degree of delocalisation. When inner 1s electrons are dislodged, the energy losses are in fact localised. Indeed, even for ultrarelativistic particles ($v = c$), $\Delta x = 0.66$ nm for the transfer of the energy $\Delta E = 300$ eV (i.e. an energy greater than the ionisation potential of the $K$ shell of the carbon atom) according to Eqn.(28), while in the transfer of $\Delta E = 500$ eV (an energy of the order of magnitude of the ionisation potential of the $K$ shell of the oxygen atom) we obtain $\Delta x = 0.40$ nm.

**Table 3.** The degrees of delocalisation in the transfer to the medium of the energy $\Delta E = 15$ eV by an electron having an energy $E_e$.[76]

| $E_e$, eV | $10^3$ | $10^4$ | $10^5$ | $10^6$ | $10^7$ | $10^8$ | $10^9$ |
|---|---|---|---|---|---|---|---|
| $10^{-8}v$, cm s$^{-1}$ | 5.93 | 18.7 | 58.5 | 164 | 282 | 300 | 300 |
| $\Delta x$, nm | 0.26 | 0.82 | 2.56 | 7.2 | 12.3 | 13.1 | 13.1 |

However, for small losses, which accompany the majority of inelastic scattering steps, the degree of delocalisation can be very considerable. In ionisation most of the dislodged electrons have low energies. The quantity $\Delta E = 15$ eV can be adopted as the most probable energy loss. The results of the calculation of $\Delta x$ for $\Delta E = 15$ eV and different energies of the incoming electron are presented in Table 3. Evidently, for relativistic electrons, the degree of delocalisation of the ionisation step is not less than 13.1 nm, i.e. is very considerable. In the excitation of an electronic state with an energy of 7.5 eV, the degrees of delocalisation are greater by a factor of 2 than those quoted in Table 3.

Thus the delocalisation region can embrace several tens of molecules of average size. Although subsequently the energy is localised at one of the molecules, it is random and the coordinates of the ionisation or excitation points cannot therefore be determined with an accuracy greater than to within $\Delta x$.

According to inequality (28), the degree of delocalisation depends on the velocity of the particle. For this reason, the values of $\Delta x$ quoted in Table 3 for heavy particles correspond to correspondingly large energies, amounting to $E = (M/m)E_e$. Thus the proton has the velocity $v = c$ for $E \geqslant 2$ GeV.

The second cause of the delocalisation of energy losses is the collective character of the excited states, which can obtain even in the excitation of the electronic states of a single molecule. The simplest example is the excitation of $\pi$-electronic states, which are delocalised along the molecule. A fast electron, exciting such a molecule, transmits energy to the entire assembly of $\pi$ electrons. As a result, the site of the excitation energy transfer is delocalised along the molecule, which can be fairly long, for example, in the case of a polymer.

The excited electronic states in molecular crystals are also collective owing to periodic symmetry. These are the thoroughly investigated exciton states.[77] The energy of the exciton state is close to the energy of the discrete electronic states of isolated molecules (4–8 eV), but in these states the excitation embraces a greater number of molecules. Under these conditions, the excitation migrates effectively in the crystal over distances up to 100 nm.[77,78] Thus owing to effective migration the excitation of one of the units of the polymer chain spread rapidly along the chain.[79] The high efficiency of such energy migration has been confirmed experimentally:[80] the saturation of the phosphorescence of luminescent additives in polystyrene on $\beta$-irradiation has been observed for a 1 : 1 ratio of the concentration of phosphor species and macromolecules, i.e. in the presence of one phosphor species per macromolecule.

Thus the excitations of discrete electronic states ($\Delta E_n < I_1$) in polymer molecules and molecular crystals are known to be delocalised. Collective excited states occur not only in crystals but also in liquids and polymer films when fast charged particles pass through them (see Section IV). The energy of such states as a rule exceeds the first ionisation potential and amounts to 15–25 eV.

It has been shown[76] that the linear size of the collective excitation region is determined by the expression

$$b_{pl} = \pi v/\omega_r = \pi\hbar v/\Delta E_r, \qquad (29)$$

where $\omega_r$ is the resonance frequency calculated by Eqn.(25). The maximum size of the region corresponds to $v = c$ and is $b_{pl}^{max} = \pi\hbar c/\Delta E_r$. For water, $\Delta E_r = \hbar\omega_r = 21.4$ eV,[66] which yields $b_{pl}^{max}(H_2O) = 29$ nm.

Thus, in the initial period of approximately $10^{-16}$ s, the energy transferred by the fast charged particle is delocalised both as a consequence of the quantum-mechanical uncertainty principle and as a consequence of cooperative effects.

As a result of the delocalisation along the direction of motion, caused by the uncertainty principle, the coordinates of the excitation and ionisation points can be determined with an accuracy to within a quantity not exceeding $\Delta x$, specified by Eqn.(28). For relativistic electrons, $\Delta x$ is fairly large and includes several tens of molecules. Thus $\Delta x = 26$ nm for the excitation of the $\Delta E = 7.5$ eV level. This factor is especially important for biological systems characterised by a marked non-uniformity as regards their sensitivity to radiation. The size of the target in radiobiology should not be

less than 10–25 nm (the spread being determined by the value of $\Delta E$ leading to the biological effect).

As shown above, the linear size of the collective excitation region of the plasmon type can reach 30 nm. Since the oscillator strengths are concentrated in the region of the peak maximum in the presence of collective peaks, the plasmon absorption is fairly considerable. It follows from the form of the energy loss function in water[66] that the plasmon absorption leads to a decrease of the fraction of the oscillator strength corresponding to transition to discrete excited states compared with their distribution in water vapour. Since the collective excitation of the plasmon type is dissipated mainly via energy transfer to a single molecule with subsequent ionisation, the "pumping" of energy from discrete excitation levels to collective excitation levels should entail an increase of the contribution of ionisation in the liquid phase compared with the gas phase. At the same time the dissipation of collective excitations can serve, as emphasised by Voltz,[81] as an additional source of superexcited states (see Section III). In the case of SES there is competition between predissociation and autoionisation. For the excitation of the SES in the course of the dissipation of the collective excitation, it is essential that the energy liberated in this process should be located in the region of the formation of the SES for the given type of molecules.

In conclusion we shall consider the consequences of the delocalisation of the excited electronic states in long molecules and of the effective migration of the electronic excitation along a polymer chain.[79] This should result in the preferential rupture of the weaker chemical bonds and also chemical bonds in the vicinity of an impurity or chain defects, since the excitation energy is localised at precisely these sites. Track effects arising from the energy transmitted to the electrons of the medium should not be manifested in such a polymer matrix, because the energy absorbed is rapidly dissipated throughout the electronic subsystem. Here there is a clear analogy with metals, where the electron gas dissipates the absorbed energy throughout the bulk of the metal without the formation of linearly extended tracks.

## VI. THE STRUCTURE OF THE TRACKS OF CHARGED PARTICLES

### 1. Tracks of Fast Electrons

Owing to its interaction with atoms and molecules on passing through the medium, a fast electron loses energy not continuously but in individual portions. The probability of such an energy loss step depends on the type of the excited state and energy of the electron (see Section II). It follows from the spectra of the energy losses arising when fast electrons pass through thin films that the most probable energy loss is 15–30 eV.[6] The transferred energy is used in the formation of ions and secondary electrons and also in the excitation of the molecules of the medium. The ions and excited molecules formed are localised in the vicinity of the trajectory of the primary electron and constitute its track.

The distance traversed by the primary electron between the energy transfer steps is referred to as the free path $l$. The mean $\bar{l} = (n\sigma_{tot})^{-1}$, where $\sigma_{tot}$ is the overall inelastic scattering cross-section and $n$ the density of the molecules of the medium. For a fast electron, up to $E > 10$ keV, $\bar{l}$ greatly exceeds the size of the region where the energy transmitted to the medium is localised. For example, for a relativistic electron in water, we have $\bar{l} = 200$–$300$ nm. Consequently a fast electron forms a series of non-overlapping microregions along its path, consisting of excited and ionised molecules.

The evolution of ideas about the structure of the fast electron track has been considered in a review[6] and in another publication.[7] Mozumder and Magee [84,85] introduced a classification of the energy structures of the track. According to this publication, the energy of the fast electron is consumed in the formation of "spurs" with energies of 6–100 eV, the so-called "blobs" with energies in the range 100–500 eV,† and "short tracks" with energies in the range 500–5000 eV.

The probability that an energy of 20 eV is localised in the spurs is highest.[85] Such spurs contain, as a rule, one ion pair (with a probability of approximately 0.5).[87] The average number of ion pairs in the spur is approximately 1.78 according to Magee and Chatterjee[87] for an average energy in the spur of approximately 30 eV. The maximum energy of the short track (5 keV) is determined from the condition for the overlap of the spurs. Short tracks consist of cylindrical regions with an enhanced concentration of excitations and ionisations and an energy distribution which can be found from the Rutherford formula [Eqn.(1)].

A numerical computer experiment with the aid of the Monte Carlo method is used to find the degradation spectrum and the energy structure of the fast electron track.[88–90] The degradation spectrum and a series of other energy characteristics of the track of a monochromatic electron beam with $E = 10$ keV in water have been found.[89,90] The authors used quantities employed for the gas phase as the interaction cross-sections, i.e. the specific features of the condensed phase were disregarded.

In a condensed phase it is difficult to separate the interaction of an electron with an isolated molecule. For this reason, instead of the molecular excitation cross-section $\sigma_k(E)$, one usually employs in this case the reciprocal of the free path $l^{-1} = n\sigma_k(E)$ in relation to the excitation in the $k$th state and the cross-section itself is expressed as a function of the energy losses $\mathrm{Im}[-1/\varepsilon(\mathbf{q}, \omega)]$ (see Section IV).

The tracks of an electron with $E_0 = 1$ and 10 keV in water have been modelled.[71,91,92] However, since the dependence of the dielectric constant function $\varepsilon(\mathbf{q}, \omega)$ on $\mathbf{q}$ is unknown, it was modelled using data for the gas phase. The role of the phase state in primary radiolytic processes has been investigated in a study[91] where the overall radiation ionisation and excitation yields and the degradation spectrum of the electrons in water and water vapour were found.# The evolution of the track of a fast electron in water for times up to $10^{-7}$ s has been investigated[92] by the computer modelling method.

For a more detailed investigation of the influence of the structure of the track on radiation-chemical reactions, it is necessary to know not only the energy characteristics of the track but also the spatial distribution of the secondary electrons and the excitation and ionisation steps throughout the bulk of the track. The Monte Carlo method is also

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† The upper limit to the energy of the blob is extremely arbitrary. In a recent study by Magee and Chatterjee[86] the upper limit was assumed to be 1600 eV.

# In a communication by the authors of this review and V.Ya.Sukhonosov, a comparative study of the primary stage of the radiolysis of water in the gas and liquid phases is described: for a brief description of the results, see Ref. 170.

convenient for the determination of this distribution. Studies of this kind have been carried out.[91–95]

The so-called "stochastic" approach, in which an instantaneous picture of the spatial distribution of the excitation and ionisation steps is fixed, has been used in investigations[93,94] of electron tracks. In this case the tracks constitute a set of points in space where inelastic scattering steps have taken place. Having at one's disposal sets of such tracks, it is possible to calculate the spectrum of the absorbed energy in the sensitive regions of the irradiated medium[93] and to calculate their line shapes and the decay of the electronic spin echo signals.[94,95]

When the velocity of the electron exceeds the velocity of light in the medium, an additional source of energy losses, namely the Vavilov–Cherenkov radiation, appears. The contribution of this radiation to radioluminescence has been fairly clearly identified in a series of investigations[96–99] and its role in photoradiation processes has been analysed.[100,101] It has been shown that the number of quanta of such radiation generated on irradiation in the accelerators employed in radiation chemistry is comparable to the light flux from the lamps employed in photochemical experiments. Thus, when photosensitive media are irradiated in accelerators, internal photoradiation processes are inevitable. Since the yield of the Vavilov–Cherenkov radiation is much lower on irradiation with a $^{60}$Co source, the irradiation of photosensitive media in an accelerator should be more effective for the same dose.

## 2. Energy Losses by Pre-excitation Electrons

Since the energy of these electrons is insufficient for the excitation of the electronic states, their energy is consumed in the excitation of vibrational and rotational states and also in inelastic collisions. In polar liquids there is an additional energy loss in dipole relaxation. In the condensed phase the energy losses are determined by the dependence of the dielectric constant of the medium on the frequency and are expressed in terms of the energy loss function $\mathrm{Im}[-1/\varepsilon(\omega)]$ [see Eqn.(16)].

In the range of energies from 5 to 0.5 eV, the resonance process involving the formation of negative molecular ions by the capture of an electron with subsequent ionisation or dissociative ionisation has large cross-sections.[102,103] According to Schulz,[104] such resonances or short-lived states of the negative ion can be divided into two groups. These are in the first place potential shape resonances which arise following the capture of an electron by the potential well formed in the electronic ground state of the molecule as a result of the centrifugal or polarisation forces. The life-span of such states is $10^{-15}$–$10^{-10}$ s. The Feshbach resonances, whose appearance is associated with the excitation of one of the electrons of the molecule, belong to the second group. This results in the formation of a state which is energetically more favourable for the addition of an excess electron. A Rydberg state may be frequently an excited state of this kind.[105] The decomposition of the negative ion formed is as a rule accompanied by the excitation of the molecular vibration. The characteristic energy loss peaks for electrons with energies in the range 0.5–3 eV when they pass through thin films have been interpreted in terms of a resonance energy loss mechanism which involves the formation of an intermediate negative ion.[106–108]

An important characteristic in the study of the pre-excitation electron retardation processes is the thermalisation distance $l_{th}$. It is essential to know this quantity in determining the size of the spur and the yield of the free ions. The first estimates of the thermalisation distance and time ($t_{th}$) for slow electrons were made by Samuel and Magee[109] who used for this purpose the classical method based on the random movement of the electron in the Coulombic field of the parent ion. Assuming that the electron traverses identical distances $l$ between collisions in the course of the retardation process and that it loses the same energy $\Delta\varepsilon$ in each collision, the authors obtained $t_{th} \cong 2.83 \times 10^{-14}$ s and $l_{th} = 1.2$–$1.8$ nm for an electron with an energy of 15 eV. Since the electron cannot overcome the attraction of the parent ion for such a low value of $l_{th}$, it is captured by the ion after approximately $10^{-13}$ s, which results in the formation of a neutral molecule in an excited state which is capable of dissociation. However, the experimental yield of the free ions showed that some of the electrons are removed to considerable distances from the ion in the thermalisation process and do not recombine.

The retardation of slow electrons in a condensed medium has been studied theoretically by Frohlich and Platzman[110] taking into account the dielectric properties of the medium. Within the framework of classical electrodynamics, they obtained an expression for the rate of energy loss by an electron moving along a linear trajectory at a velocity $v$. This expression in fact represents the non-relativistic analogue of the Fermi formula:[111]

$$-\frac{dE}{dt} = \frac{2e^2}{\pi v^2}\int_0^\infty \omega\,\mathrm{Im}\left[-\frac{1}{\varepsilon(\omega)}\right] xK_0(x)K_1(x)\,d\omega, \qquad (30)$$

where $x = \omega b_{\min}/v$ and $b_{\min}$ is the minimum impact parameter, which is assumed equal to either the intermolecular distance $d$ or to the de Broglie wavelength of the electron $\lambda$ when $\lambda < d$. Since the form of the function $\mathrm{Im}[-1/\varepsilon(\omega)]$ was not known over a wide range of $\omega$, the authors[110] confined themselves to the calculation by Eqn.(30) of the energy losses only in dipole relaxation and obtained $-dE/dt \cong 10^{13}$ eV s$^{-1}$ for water, which is independent of the electron energy in the experimental range from 1 to 10 eV. This value of energy losses was shown by the authors to be comparable to the energy losses in the excitation of vibrations.

The contributions of various mechanisms to the energy losses have been analysed.[112,113] According to the results of Magee and Helman,[112] the main contribution to the overall energy losses comes from the energy consumed in dipole relaxation (provided that such losses occur). They amount to approximately $1.5 \times 10^{13}$ eV s$^{-1}$ for water, while the energy lost in vibrations in the infrared range amounts to only approximately $10^{12}$ eV s$^{-1}$. The opposite result was obtained by Byakov and Grishkin,[114] who showed that the main contribution to the retardation of the pre-excitation electron comes from the resonance losses in the excitation of retarded longitudinal vibrations of the water molecules. An approximate analytical formulation of the function $\mathrm{Im}[-1/\varepsilon(\omega)]$ was used[114] in the calculation of the energy losses by Eqn.(30). A more accurate calculation by Eqn.(30), carried out by Garin and Byakov[115] using the experimental optical properties of water, confirmed the general conclusion drawn in the previous study.[114]

According to the results of Garin and Byakov,[115] the resonance losses resulting from intramolecular vibration in the infrared range make the main contribution to the retardation of the excitation electrons in polar liquids. The contribution of the losses in dipole relaxation proved to be smaller by an order of magnitude. This conclusion is more valid for non-polar liquids, where the main channel for these losses is not the relaxation of permanent dipole moments (the latter are zero) but the dipole moments induced in the molecules of the medium by the passing electron. As a result, the electron retardation time in the majority of liquids is

determined by the resonance absorption in the infrared range. Liquids made up of molecules with a high symmetry, which have no active vibrations in the infrared range, for example the molecules of methane or neopentane, may constitute exceptions.

According to Garin and Byakov,[115] the rate of energy loss by an electron having $E = 7.5$ eV in Debye relaxation is $(-dE/dt)_D \cong 10^{12}$ eV $s^{-1}$ and the overall rate of resonance losses is $(-dE/dt)_r \cong 4 \times 10^{13}$ eV $s^{-1}$. The maxima in the region of molecular librations ($\bar{\nu} \cong 700$ $cm^{-1}$) and the intramolecular stretching vibations ($\bar{\nu} \cong 3400$ $cm^{-1}$) make the main contribution to the resonance losses. As a consequence of the increase by a factor of approximately 2 of the reduced masses in stretching vibrations in $D_2O$, the rate of energy loss should be lower by a factor of 2 and the retardation time and the path traversed should therefore be greater by a factor of 2. This conclusion agrees with the results of recent measurements.[116]

The energy barriers had been calculated earlier[117] by Eqn.(30) taking into account the experimental values of $\mathrm{Im}[-1/\varepsilon(\omega)]$. The data obtained in the above studies[115,117] for the overall energy losses by slow electrons agree. However, Raitsimring et al.[117] failed to analyse the contribution of the individual mechanisms to the retardation of slow electrons. On the other hand, they calculated the total thermalisation distances for water, ice, and benzene.

Calculation by Eqn.(30) makes it possible to estimate the energy losses in the course of the linear movement of an electron. The curvature of the trajectory has been taken into account with the aid of the Monte Carlo method[112,113] and analytically.[118] Mention should also be made of the fact that Eqn.(30) does not allow for the energy losses in close collisions of an electron with molecules, including the formation of an intermediate negative ion. The contribution of close collision processes to the energy losses has been estimated by Magee.[113] For water, the contribution of these processes to the rate of energy loss by an electron with $E = 1$ eV amounted to approximately $5 \times 10^{13}$ eV $s^{-1}$, while in paraffinic hydrocarbons it amounted to approximately $7 \times 10^{13}$ eV $s^{-1}$. Consequently, among all the mechanisms responsible for the retardation of slow electrons, it is difficult to isolate one which would be of decisive importance over the entire thermalisation distance.

Even when account is taken of the energy losses in close collisions, Eqn.(30) does not allow an adequate determination of the thermalisation distance. Electrons with an energy below the vibration excitation threshold are subjected to fairly effective elastic scattering. In the calculation of energy losses via elastic scattering one can as a rule neglect the energy transferred to effect the collision in view of its low value. On the other hand, the contribution of the elastic scattering to the thermalisation distance is comparable and perhaps even greater than the contribution of the inelastic collisions.

Thus it proved difficult to obtain direct information about the thermalisation distance by direct procedures. In a number of studies, for example those in Refs.119–121, the effective thermalisation distances were therefore determined from the distribution functions for electron pairs with respect to distances. These functions were found from the yields of the free ions either in the absence of a field or for low electron field strengths. However, the values obtained in this way are unreliable because the yield of the free ions is only weakly sensitive to the changes in the thermalisation distances.

After the development of a method for the investigation of photoemission phenomena at the metal–solution boundary,[122–124] the direct experimental determination of the thermalisation distances of free electrons became possible (see the studies quoted above and also Refs.116 and 125–127). The path traversed by an electron with $E \cong 3$ eV proved to be approximately 5 nm in $H_2O$ and approximately 10 nm in $D_2O$.[116] For comparison, we may note that the ionisation path of an electron with $E = 100$ eV in water is approximately 1.5 nm, i.e. is much shorter than the thermalisation distance). In a review by one of the present authors[47] it was stated in the discussion of the form of the function $l(E)$ obtained by Raitsimring et al.[125] that it was essential to explain the absence of the dependence of $l$ on $E$ for $E < 2$ eV. In a recently published study[116] a monotonic decrease of $l(E)$ as the electron was retarded was obtained for $D_2O$, while for $H_2O$ there is a plateau in the energy range $E = 1$–$2$ eV. However, it has been correctly stated[116] that, owing to the lack of data for the energy distribution of photoelectrons on excitation of the cathode, it is premature to carry out a detailed interpretation of the results.

After the electron has been thermalised, it can either recombine with a positive ion (not necessarily the parent ion) or it can be captured by a trap. The traps can be not only molecules with a positive electron affinity but also structural defects in the medium or polarisation wells formed when an electron interacts with the surrounding molecules. Such a captured electron has come to be referred to as solvated (hydrated in water). Since very numerous monographs and reviews have been devoted to the solvated electron,[128–130] we shall not deal with these questions. We may note that the theory of the solvated electron is still far from complete.[131]

Numerous studies have also been devoted to the behaviour of the excess electrons induced by irradiation in non-polar solutions and solid matrices (see the relevant reviews[132–134]). It has been established that the excess electrons exist in the medium in two states: localised and quasi-free. Their ratio depends on the nature of the molecules, especially on their symmetry: the higher the symmetry (for example, in neopentane) the greater the fraction of electrons in the quasi-free state.[135]

### 3. The Structure of the Tracks of Heavy Ions

Among the entire multiplicity of interactions of heavy ions in a medium, the most effective over a large part of the path traversed are, as in the case of fast electrons, the inelastic interactions with the electrons of the medium (electron retardation). Only at the end of the path does the role of elastic interactions with the atoms of the medium and the electron capture and loss processes (charge transfer) increase. The role of the latter processes becomes more pronounced with increasing mass of the ions.

The process in which the energy of the ion is transferred to the electrons of the medium is independent of the mass of the ion and its probability is proportional to the ratio $Z^2/v^2$. The size ($\Delta x$, $b_{\mathrm{eff}}$) of the region where the energy transferred to the medium in glancing collisions is localised is fully determined by the velocity of the charged particle. Hence it follows that a heavy ion generally speaking generates the same track structures as a fast electron having the same velocity $v$. The specific features of the transfer of the energy of the ion and of its distribution in the medium are manifested by the following factors.

A heavy ion is capable of dislodging an electron with a maximum energy $\varepsilon_{\max} \cong 2mv^2$ on ionisation, while in the case of a fast electron having the same velocity $\varepsilon_{\max} = \frac{1}{2}mv^2$. Consequently in head-on collisions, where the energy transferred $\Delta E \cong \varepsilon_{\max}$, this fraction of the energy is distributed

over larger distances from the site of the primary ionisation than in the collision of electrons having the same velocity.

Since the energy losses and the change in the momentum of the primary heavy ion in individual collisions with electrons of the medium constitute small fractions of the energy and moment of the ion ($\Delta E_{max}/E_0 \cong 4m/M < 2 \times 10^{-3}$), the electron retardation has only a weak influence on the curvature of the trajectory of the ion. For this reason, in the part of the track where ionisation losses predominate, the trajectory of the heavy ion can be regarded as linear.

The strength of the interaction of the ion with the medium is proportional to the square of its charge $Z^2$. The increase of the charge leads to an increase in the energy transferred to the medium in individual energy loss steps and also in the average energy loss per unit length of the path and of the number of electrons. On the other hand, an increase in $Z$ entails a diminution of the mean free path (because $\sigma_i \propto Z^2$). For this reason, the overlap of the track structures as the ion is retarded occurs earlier for ions with higher values of $Z$.

The proton and α-particle have the constant charge $Z$, equal to the nuclear charge $Z_a$, over most of their path so long as their velocity is sufficiently high. In multicharged ions (for example, in fission fragments) $Z$ is as a rule smaller than the nuclear charge. As a consequence of the charge transfer processes, when a beam of ions has passed through a sufficiently thick layer of the given substance, the ions show a distribution of charges. This distribution is characterised by an average quantity—the effective charge $Z_{eff}$, which is adopted as $Z$ in the calculations of ionisation energy losses. When the velocity of the ion $v \ll Z_a^{3/4} v_0$, the expression

$$Z_{eff} = \eta Z_a^{1/4} v/v_0,$$

where $v_0 = e^2/\hbar$ is the velocity of the electron in the first Bohr orbital and $\eta$ a constant which depends on $Z_a$ and the properties of the medium,[136] is valid for $Z_{eff}$. If $Z$ is now replaced by $Z_{eff}$ in Eqn.(13), then the dependence on the velocity of the ion in the multiplier of the logarithm disappears and it remains only in the logarithmic term. As a result, as the multicharged ion is retarded, its ionisation losses diminish in accordance with a logarithmic law. It will be shown below that this feature is manifested in the specific characteristics of the structure of the track of a multicharged ion.

At high velocities the track of a heavy ion can be regarded as consisting of individual track structures resembling the track structures of a fast electron. However, in radiation chemistry one deals with ions whose initial velocity does not as a rule exceed 10 MeV per nucleon. For initial energies of this kind, the velocity of the ions is less than $4 \times 10^9$ cm $s^{-1}$; the spurs overlap over most of the lengths of the track giving rise to a region of continuous ionisation along the paths traversed. The inner part of this region, which is characterised by an increase in the density of ionisations and excitations, has come to be referred to as the core. For low velocities of the ion, the radius of the core has been assumed[137] to be 1 nm. This value was chosen on the basis of the condition for the retardation of secondary electrons with an energy of 100 eV.

Part of the energy of the secondary electron is absorbed in the core of the track. Only high-energy δ electrons are capable of moving outside the limits of the core and of forming individual track structures. When the tracks of electrons overlap, a continuous shell surrounding the core, narrowing towards the end of the track, is produced.[138]

The distribution of ionisation excitation steps effected by secondary electrons has been studied in many investigations. The Monte Carlo method proved to be the most effective for detailed study.[139-141] The spatial distribution of the ionisation steps and the change of the energy distribution of the δ electrons as a function of the distance from the axis of the track and along the track have been investigated.[140] The data obtained can be used to compare the structures of the tracks of ions of different kinds with specific energies ranging from 82 to 420 keV per nucleon. Table 4 presents the results for the tracks of the α-particle and the multicharged $^{127}I$ ion in water. Evidently the geometrical dimensions of the tracks of ions having identical velocities are equal. However, the qualitative structure of the core and the dependence of the characteristics of the track of a multicharged ion on the linear energy transfer (LET) are different from those in the track of the α-particle (or the proton).

**Table 4.** Characteristics of the tracks of α-particles and the multicharged $^{127}I$ ion in water*.

| Characteristic of track | $10^{-8}v$, cm $s^{-1}$ | | | | |
|---|---|---|---|---|---|
| | 9 | 7 | 6 | 5 | 4 |
| $E$, MeV | 1.7 | 1.0 | 0.75 | 0.5 | 0.3 |
| | 53 | 32 | 24 | 16.5 | 10 |
| $S_e$, eV $nm^{-1}$ | 168 | 212 | 230 | 240 | 252 |
| | 6000 | 5540 | 5240 | 3600 | 3210 |
| $Z_{eff}$, e | 1.85 | 1.68 | 1.58 | 1.47 | 1.38 |
| | 11.0 | 8.6 | 7.4 | 6.0 | 5.0 |
| $N_\delta$, $nm^{-1}$ | 3.3 | 4.5 | 5.0 | 5.7 | 6.7 |
| | 118 | 118 | 117 | 87 | 84.5 |
| $N_i$, $nm^{-1}$ | 5.2 | 6.8 | 7.4 | 7.9 | 8.4 |
| | 190 | 177 | 168.5 | 118 | 107 |
| $10^{-21}\bar{n}_i^c$, $cm^{-3}$ | 1.46 | 2.0 | 2.18 | 2.4 | 2.66 |
| | 52.6 | 52.3 | 51 | 36.6 | 33.7 |
| $10^{-19}\bar{n}_i$, $cm^{-3}$ | 0.27 | 0.54 | 1.0 | 3.8 | 7.4 |
| | 9.7 | 14.0 | 23.8 | 58.7 | 94 |
| $r_{max}$, nm | 25.0 | 20.0 | 15.0 | 8.0 | 6.0 |

*The values of each parameter for the α-particle and the multicharged ion are given in the upper and lower rows respectively; $N_i$ and $N_\delta$ are the number of ions and δ electrons formed by the particle over 1 nm of the length of the track respectively, $\bar{n}_i^c$ is the average concentration of ions in the core of the track, $\bar{n}_i$ the average concentration of ions in the track, $r_{max}$ the maximum radius of the track, and $v_i$ the velocity of the ion.

As already mentioned above, owing to the effective neutralisation of the charge as the multicharged ion is retarded, its LET falls in the range of energies where ionisation losses predominate. Nevertheless, in view of the fact that the radius of the track contracts faster than the rate at which LET diminishes on retardation of a multicharged ion, the average concentration and yield of the primary ions in the track of such an ion behave in the same way as in the track of the α-particle, i.e. they increase with decrease in the energy of the ion. This increase continues up to energies at which the losses in elastic collisions become comparable to ionisation losses (i.e. up to $v \cong 4 \times 10^6$ m $s^{-1}$).

As a result of the primary effects, the multicharged ion ionises virtually all the molecules contained in a cylinder 0.7 nm in diameter (see the relevant estimates[138]). Most of

the energy of the secondary electrons is also localised in the core of the track. As a consequence of this, the number of ionisation steps in the core of the track of a multicharged ion exceeds the number of molecules. Thus almost every molecule in the core undergoes repeated ionisation and excitation processes and hence dissociates into fragments. For this reason, the region adjoining the axis of the track of a multicharged ion (with a radius of 1 nm) consists of a cylindrical ion core filled mainly by fragment ions. It has been shown[142] that at the end of the physical stage of the inhibition process the core of the track of the multicharged ion consists of a low-temperature, non-isothermal, spatially unlimited non-ideal plasma (an analogous conclusion was reached later by Ritchie and Claussen[143]). The individual components of such a plasma chain exist in local quasi-equilibrium states (for further details, see Miterev[142]). The processes in such tracks proceed under significantly non-equilibrium conditions where it is impossible to introduce a single temperature for all the degrees of freedom of this molecule. As a result, the usual ideas concerning the reaction rate constant lose their significance. In describing the processes in the track of multicharged ions, one must employ the methods of plasma chemistry.[144]

## VII. CHARACTERISTICS OF THE RADIATION-CHEMICAL REACTIONS IN THE TRACKS OF PARTICLES OF DIFFERENT KINDS

### 1. The Influence of the Phase States and the Role of the LET in Radiolysis

In a gas the track structures contain as a rule a small number of active species which are separated by large distances from one another. As a consequence of diffusion, the initial non-uniformity in the distribution of active species rapidly smoothes out and at the beginning of chemical reactions the intermediate species are distributed almost homogeneously throughout the volume. For this reason, the role of tracks in the gas phase is negligible. Only when the gas is acted upon by multicharged ions such as fission fragments can spatial non-uniformity influence the chemical reactions.[145,146]

The spatial non-uniformity in the distribution of the reactions in a liquid is more marked owing to the greater density of this medium. On the other hand, diffusion processes in liquids are slower. Furthermore, the phase state of the medium has an effect on the redistribution of the primary active species (increasing the number of ionised states in the liquid—see Section V) and also on the subsequent relaxation processes and the decomposition of the excited and ionised states.[147] The role of the reverse processes involving the recombination of electrons with the parent ion becomes more pronounced on passing from a gas to a liquid and the degree of decomposition of molecules into radicals as a consequence of the so-called cage effect diminishes.[148]

The differences between the kinetics of the gas- and liquid-phase reactions, which depend on many factors, preclude the differentiation in a pure form of the role of tracks by altering the density of the medium. The most fruitful procedure apparently involves the study of the dependence of the radiation effect on the structure of the track for constant physical and chemical properties of the medium.

One of the characteristics of radiation (and its ionising capacity) is the linear energy transfer. Quantitatively LET is equal to the average energy transferred to the medium when the ionised particle traverses a unit length of its path. For fast particles, the LET is virtually equal to the ionisation losses. It has come to be assumed that the higher the LET the higher the density of the chemically active species in the track and the greater the probability of the reactions of the active species with one another rather than with the molecules of the solute.[149-151] Thus the increase in the yield of molecular hydrogen and the decreased yield of electrons stabilised in the free radicals with increase of the LET in the radiolysis of water are well known.[152,153] The study of the radiolysis of some organic substances also produced data indicating an increase with increasing LET of the yield of molecular products, whose formation can be explained by the recombination of chemically active species, for example, radicals in the tracks.[154]

Calculations for the radiolysis of liquids are carried out by solving the equations of the diffusion-dependent kinetics of radiation-chemical reactions in tracks.[155-158] The use of ideas about the track structures with spherical or cylindrical formations and the application of the equations for diffusion-dependent kinetics explained many experimental facts observed in the radiolysis of aqueous solutions,[156,159,160] in particular, the dependence of the yield of products on the LET. As a result of this factor, LET came to be regarded as a universal characteristic of the quality of the radiation on the assumption that the concentration of the active species in the track depends directly on the LET without taking into account the type of the charged particle.

However, many experimental results obtained in the study of the dependence of the yields of the radiolysis products of organic liquids on the LET failed to find a new theoretical justification within the framework of the existing ideas about the relation between the structure of the track and the LET. Among such experimental facts, one may specify the following: a sharp increase in the yield of low-molecular-weight radiolysis products for high values of LET;[161,162] an increase in the yield of a series of products of the radiolysis of methanol (for example, ethylene glycol[163]), whose formation is attributed to the recombination of radicals in the tracks, with decrease in the LET; the difference between the yields of hydrogen $G(H_2)$ in the radiolysis of benzene by protons and $\alpha$-particles having identical values of the LET.[164]

In order to explain all these experimental results, it was necessary to resort to the concept of the detailed structure of the track and its dependence on the type of the charged particle.[5]

### 2. The Influence of the Structure of the Track on Radiation-Chemical Processes in Liquids

The role of the structure of the track has been traced most clearly in relation to the radiolysis of liquids by heavy ions. Precisely in this case it is possible to vary within wide limits the geometrical dimensions of the tracks and the concentrations of the active species in them. The influence of the structure of the tracks of ions has been investigated by Burns[164,165] and also by Kaplan and Miterev.[5]

Using detailed ideas about the structure of the tracks of ions, it is possible to account for the dependence of the yields of products on the LET in the following way.[5] Low values of LET are characteristic of the radiolysis of liquids on irradiation by high-energy protons. The track of the proton consists in this case of a core and branches—the tracks of $\delta$ electrons, and the higher the energy of the proton the greater the proportion of its energy removed outside the limits of the core by $\delta$ electrons. The core itself is ultimately transformed into individual non-overlapping spurs, i.e. the track of the proton resembles that of

the electron with the exception of certain features (see Section VI). As a result, the character of the radiolysis approaches that of the radiolysis by fast electrons.

As the proton is retarded, its LET and the number of δ electrons increase, while the size of the track actually diminishes, because the maximum energy of δ electrons falls. This results in a sharp increase of both the local and average concentrations in the vicinity of the axis of the track. This tends to increase the yields of the products of the recombination of the active species with increasing LET, i.e. there is a direct correspondence between the density of the active species in the track and the LET. An analogous picture has been observed in the tract of the α-particle.

High values of LET (in excess of 1 keV $min^{-1}$) are observed when a liquid is acted upon by multicharged ions, such as fission fragments. As already mentioned in the previous Section, the structure of the tracks of such ions has a number of characteristic features. The first of these is associated with the fact that the average concentration of active species increases with increasing LET. For this reason, the yields of many radiolysis products initially increase with decrease in the LET of the fragment, reach a maximum, and then (when in the course of further retardation of the fragment the energy losses in elastic collisions become significant) they dimish. The experimental results for the radiolysis of methanol by fission fragments having different energies can be accounted for in precisely this way.[163]

The second characteristic feature of the structure of the track of a multicharged ion is a high concentration of fragment ions in the core of the track manifested by the fact that mainly low-molecular-weight radiolysis products are formed in the core of the track, while the yields of products with a more complex structure diminish. The high yields of $H_2$, CO, and $CH_4$ in the radiolysis of liquid hydrocarbons by multicharged ions are associated with this fact.[161,163,164]

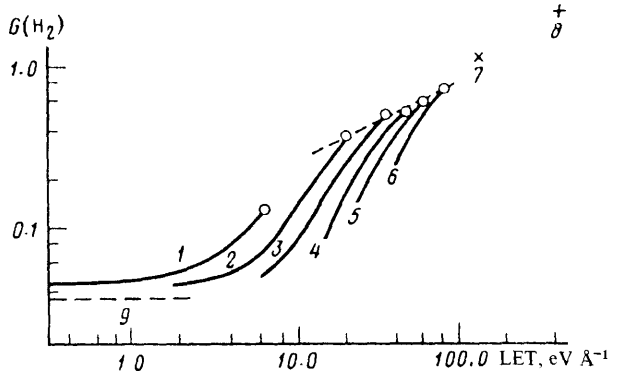



**Figure 5.** Dependence of the differential yield of molecular hydrogen $G(H_2)$ on the LET in benzene for different ions: 1) $^1H$; 2) $^4He$; 3) $^7Li$; 4) $^9Be$; 5) $^{11}B$; 6) $^{12}C$; 7) $^{20}Ne$; 8) fission fragments; 9) fast electrons.[166]

The intermediate values of the LET correspond to the radiolysis of liquids irradiated by different ions. As a result, it has been found that two and more ions can have the same values of the LET (see, for example, La Verne and Schluer[166]). With the exception of the range of low energies, the LET is determined by the ionisation losses $S_e$ [see Eqn. (13)]. If the ionic charges $Z$ are different, then the equality of the $S_e$ (up to the Bragg peak) holds for different velocities of these ions. An ion with a high value of $Z$ has a high velocity $v$ and for this reason the core of its track ($r_c \propto v$) and the region adjoining the core (formed by the tracks of δ electrons) have large dimensions. As a result, the local and average concentrations of the active species in the track of such an ion are reduced.

Thus the higher the charge on the ion the greater the volume of its track in which the linear losses are distributed, i.e. the lower the local concentrations of the active species. As a consequence of this, the radiolysis seen in the track of an ion with a high $Z$ corresponds in essence to a process which is observed for lower LET in the tracks of ions with a lower charge. This behaviour is in fact observed in the measurement of the yield of $H_2$ in the radiolysis of benzene by various ions[164,166] (Fig. 5).

Thus an important conclusion follows from the analysis of the influence of the structure of the tracks on radiation-chemical processes: there is no direct correspondence between the LET and the local and average concentrations of the active species in the tracks. For this reason, the LET cannot serve as a universal characteristic of the quality of the radiation regardless of the particular species involved.

Attempts have been made to introduce instead of the LET another characteristic of the quality of the radiation, for example, the ratio $Z^2/v^2$.[167,168] However, a complete description in terms of $Z^2/v^2$ could not be achieved,[169] which can be readily explained. The factor $Z^2/v^2$ is an approximation to the LET and all the remarks referring to the use of the LET as a universal characteristic of radiation fully apply also to this parameter.

The dependences of the differential yield $G(H_2)$ on the average density of the absorbed energy in the core of the track have been compared for different ions[166] and it was found that, for the same density, the values of $G(H_2)$ depend significantly on the type of ion and hence also on the distribution of the energy (and the primary species) outside the limits of the core, i.e. they depend on the complete structure of the track.

Apparently the attempts to introduce a universal parameter characterising the radiation-chemical effect of radiation have been unsuccessful. Such a characteristic may be only the spatial distribution of active species in the track. The form of the latter throughout most of the paths of the particles is determined both by the charge $Z$ and by the velocity $v$ of the particles and not solely by their ratio. These two parameters must in fact be used as the characteristics of charged particles. For a comparative estimate of the radiation effects of various types of radiation, certain characteristics averaged over the volume of the track, such as the average energy density in the track, the average concentration of active species in the track, etc., are also useful.

The foregoing has a direct bearing on the dosimetry of the ionising radiation using liquid systems. Since the radiation effect in such systems generally speaking depends on the structure of the track of the charged particles, the determination of the dependence of the readings of liquid type dosimeters on the LET is meaningful only when a single type of radiation is used. Furthermore, the application of a dosimeter calibrated against one type of radiation in the measurement of absorbed doses of other types of radiation requires the introduction of corrections for the specific features of the track effects.

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In conclusion we may note that, in view of the multiplicity and complexity of the active primary species and intermediates formed in the radiolysis of even a thoroughly investigated

medium such as water, there is as yet no firmly established mechanism of the radiolysis in both the primary and subsequent stages. In the first place, the lack of reliable data on the cross-sections of the interactions of slow electrons with molecular media precludes the determination of a detailed spatial distribution of the primary active species in the electron tracks. The types of reactions of the primary active species in the condensed medium, namely ions, superexcited molecular states (for example, Rydberg states), and also plasmon excitations in non-metallic media, have not as yet been firmly established. The solution of these problems would make it possible to carry out calculations for the radiolytic process up to the evaluation of the radiation yields of the final products.

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# The Application of High Resolution Nuclear Magnetic Resonance in the Study of Fast Non-equilibrium Reactions

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Literature data concerning the use of high resolution NMR in the study of the mechanisms of fast non-equilibrium chemical reactions are examined and surveyed. Attention is concentrated on the methods and techniques of flow experiments in which stationary and pulsed Fourier-transform NMR is used. The possibilities and prospects for the development of these methods are analysed.
The bibliography includes 139 references.

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## I. INTRODUCTION

The greatest advances in the study of fast reactions by high resolution NMR have been made in the investigation of equilibrium processes with the aid of the dynamic magnetic resonance methods,[1-4] the saturation transfer effect,[5-8] and two-dimensional NMR.[9,10] On the other hand, the study of non-equilibrium processes, including irreversible chemical reactions, has been limited to very slow reactions with characteristic times $t_{1/2}$ in excess of 100 s.[11-14] This limitation was associated primarily with the lack of special methods for the measurement and treatment of high resolution NMR spectra for non-equilibrium reaction mixtures. At the same time there is no doubt about the likely usefulness of the application of NMR in the determination of the structures of relatively unstable intermediates in fast† chemical reactions and the determination of independent kinetic information.

The increase of the working frequency of spectrometers and the introduction of pulsed methods of recording[15] greatly increased the sensitivity and speed of NMR spectroscopy, which extended its functional possibilities for the study of rapid non-equilibrium chemical reactions in solution. The application of NMR in this field makes it possible to obtain qualitative and quantitative information about the composition of a non-equilibrium reaction mixture 0.05 s after the start of the reaction and hence permits an expansion by 3–4 orders of magnitude of the range in which it can be employed.

The large amount of information derivable from NMR spectra is one of the main factors responsible for the vigorous development of NMR methods for the rapid recording of short-lived intermediates in non-equilibrium chemical reactions. At the same time, the relatively low sensitivity of NMR prevents its being a competitor, in the determination of kinetic information, of the UV, IR, and EPR spectroscopic methods widely used for such purposes.[16-18] However, here too there has been definite progress as a result of the improvement of the methods of the kinetic NMR measurements and the development of fundamentally new methods for the determination of kinetic data.

The aim of the present review is the analysis of the methods and characteristics of the employment of NMR in the study of fast non-equilibrium reactions in solution. Two main factors are considered: the method whereby the initial non-equilibrium state of the specimen is established in the measuring cell of the NMR spectrometer and the actual NMR recording of the attainment of equilibrium in the test system. The first studies of the use of NMR in the investigation of fast irreversible reactions dealt with the effects of chemically induced nuclear polarisation (CINP),[19] electrolysis,[20] and radiolysis.[21] In order to generate the initial non-equilibrium state, appropriate exciting devices were used. However, among the special methods for the investigation of fast reactions in solution,[22] flow methods, in which equilibrium is perturbed as a result of the chemical reactions, have come to be most widely employed.[23] In most investigations the recording of the attainment of equilibrium is to some extent associated with the measurement of a high-resolution NMR spectrum in a flowing liquid. We shall therefore deal with the characteristic features of the use of an NMR spectrometer as the detecting device in flow methods for the study of fast reactions.

## II. FLOW METHODS AND NUCLEAR MAGNETIC RESONANCE IN A FLOWING LIQUID

The flow methods for the study of fast chemical reactions in solution are based on the rapid and effective mixing of the initial reactants at the mixing point and the recording of the changes in the NMR parameters as a function of time at the point where the receiving coil of the spectrometer sensor is located.

In virtually all the known studies two commonest and simplest methods have been used in one form or another, namely the continuous and stopped flow methods. The choice of one of them is associated primarily with the amount of the solution of the initial reactants available and the speed with which the observation can be made. The first of the methods is based on the establishment of a stationary composition of the reaction mixture at the recording point as a result of the uniform flow of the specimen through the spectrometer sensor and makes it possible to record the spectrum under the usual conditions. The NMR spectrum obtained in this way corresponds to the time necessary for the transport of reaction mixture after the start of the

†In $^1$H NMR, the term "fast" reaction should be understood as implying reactions occurring at room temperature with half-lives $t_{1/2} < 30$ s.

reaction ($\tau_{tr}$), which is unambiguously defined by two parameters of the flow system—the flow rate of the reaction mixture $v$ and the distance between the mixing and recording points $l$:

$$\tau_{tr} = \frac{l}{v} \quad . \tag{1}$$

When the stopped flow method is used, the amount of reactants consumed is much smaller. In this case, a selected section of the spectrum "varying" with time is rapidly scanned after the rapid arrest of the flow of the reaction mixture.

The theoretical principles of NMR in a flowing liquid, which have been described in a monograph,[24] reduce to the following: the flow of the specimen in the sensor along the y axis does not entail any frequency distortions in the NMR spectrum and is expressed by a decrease of the effective (observed) spin–lattice ($T_1^*$) and spin–spin ($T_2^*$) relaxation times. As early as 1951, an increase of the amplitude of the NMR signal was noted[25] under the conditions of a uniform movement of the liquid compared with a stationary specimen. This effect was explained[26] by the acceleration of the spin–lattice relaxation of the volume-average magnetisation of the nuclei, which takes place as a result of the flow into the sensor of the liquid with a uniform magnetisation. It was concluded that the signal amplitude in the flow sensor corresponds to the effective spin–lattice relaxation time $T_1^*$, which is related to the natural time $T_1$ by the expression

$$\frac{1}{T_1^*} = \frac{1}{T_1} + \frac{1}{\tau} \, , \tag{2}$$

where $\tau$ is the time during which a proportion 1/e of the depolarised nuclei is replaced by polarised nuclei as a result of the flow of liquid in the resonance zone (e is the base of natural logarithms).

At the same time an analogous decrease of the effective spin–spin relaxation time $T_2^*$ was observed:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{\tau} \quad . \tag{3}$$

This entails a broadening of the spectral lines. Owing to this broadening, Bloom and Shoolery[27] were unable to increase the sensitivity of high-resolution NMR spectrometers with the aid of a flow sensor and a varying working substance. Their attempt was based on the possibility of using higher powers of the microwave frequency field $H_1$ by reducing $T_1^*$ and $T_2^*$ in the flowing liquid while maintaining the value of the saturation factor $z$:

$$z = 1 + (\gamma H_1)^2 T_1^* T_2^* \, .$$

Another feature of the use of flow NMR which is of practical importance is the difficulty of ensuring the necessary equilibrium magnetisation of the liquid. Whereas for a usual specimen the equilibrium magnetisation $M_0$ is attained by placing it for a time in the field of the spectrometer magnet $H_0$, for a flowing specimen it can be achieved as a result of its being passed beforehand through a special polariser, since the time during which the specimen flows through the sensor is insufficient for the establishment of the equilibrium magnetisation. The polariser is usually placed in the space between the poles of the spectrometer magnet and, when no free space is available for this purpose, the flowing specimen is polarised with the aid of an additional polarising magnet having a field strength $H_0^{pol}$.[24]

The initial parameters in the calculation of the geometry of the polarisation coils are the spin–lattice relaxation time of the $i$th transition investigated ($T_1^i$) and the flow rate of the specimen. For a multispin system, the residence time of the flowing specimen in the polariser $t_p$ is chosen from the condition

$$t_p \geqslant 5 T_1^{max} \, , \tag{4}$$

where $T_1^{max}$ is the maximum spin–lattice relaxation time among all the values of $T_1^i$. When condition (4) holds, the Boltzmann distribution in the flow system is established to the extent of 98% and the phenomenon of nuclear magnetic resonance can be observed in it. Depending on the ratio of the reaction half-life and the value of $5T_1^{max}$, the preliminary magnetisation of the reaction mixture can be achieved both before and after mixing the initial reactants. For very short spin–lattice relaxation times, the role of the polariser can therefore be fulfilled by the section between the mixing and recording points located within the gap of the spectrometer magnet.

If the condition $H_0^{pol} > H_0$ holds when a second polarising magnet is used to polarise the flowing specimen, then an increase of the sensitivity of the spectrometer is achieved together with the magnetisation of the specimen. For sufficiently short times taken for the transport of the test specimen from the polarising magnet to the spectrometer magnet, the effective equilibrium magnetisation $M_0^{eff}(t)$ remains greater than the value of $M_0$ which can be attained in the uniform spectrometer field $H_0$. The disadvantage of this method of increasing sensitivity is that the amplification factor $K$ depends on the relaxation times of different nuclei $T_1^i$:[24]

$$K = \frac{M_0^{eff}(t)}{M_0} = \frac{M_0^{tot} \exp(-t/T_1^i)}{M_0} = K_0 \exp(-t/T_1^i) \, ,$$

which should distort the true ratio of the signal intensities in the NMR spectrum of the reaction mixture. However, since there is no need for a high uniformity of the field of the more powerful polarising magnet, these methods for the polarisation of the flowing specimen can be preferable in some cases.

Another approach to the establishment of the preliminary magnetisation in the flowing specimen consists in the artificial shortening of the spin–relaxation time of the nuclei with the aid of paramagnetic additives. However, this entails the simultaneous shortening of the corresponding spin–spin relaxation times, which leads to the broadening of the spectral lines to hundreds of gauss.[28] This disadvantage has been eliminated in a recently proposed method.[29] Owing to the interaction of the flowing liquid with the free radicals adsorbed on the solid substrate, the time necesssary for the polarisation of the specimen in the field of the spectrometer magnet is shortened in zone $A$ (Fig.1) by several orders of magnitude. It becomes comparable to the residence time of the flowing specimen in zone $A$. In the region $B$, the influence of paramagnetic centres on the width of the lines is to a large extent weakened owing to the effective filtration of the adsorbent on a glass filter. The necessary conditions for the use of free radicals in this procedure are their chemical inertness, the ease of filtration of the adsorbent, and the constancy of the concentrations in zone $A$. According to the authors,[29] the use of paramagnetic relaxants leads to the prospect that $^{13}C$ NMR experiments, which have longer spin–lattice relaxation times, may become possible.

The overall requirements which must be met by the method and technique of any flow experiments are well known.[22] These are primarily the necessity for the rapid and effective mixing of the reactants, the establishment of the laminar flow of the reaction mixture in the continuous flow method, and the rapid arrest of the flow in the stopped flow method. The main characteristic of the efficiency of the apparatus in

flow measurements is the experimental dead time $\tau_0$—the minimum time after the start of the reaction necessary to record any physical quantity. For the continuous and stopped flow methods, it includes the reactant mixing time $\tau_{mix}$ and the time required for transport to the recording point $\tau_{tr}$, while for the stopped flow method there is in addition the time necessary to stop the flow ($\tau_{st}$).

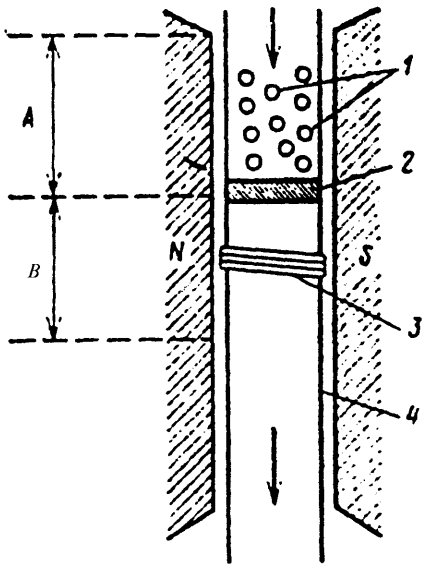



**Figure 1.** Artificial reduction of the magnetisation time of a flowing specimen by introducing stable paramagnetic centres into the recording channel in NMR flow experiments:[29] *1*) free radicals adsorbed on a solid substrate; *2*) glass filter; *3*) receiving coil; *4*) recording channel; *A*) preliminary polarisation region; *B*) recording region.

The mixing chambers developed previously for the UV, IR, and EPR methods[17,30,31] makes it possible to mix almost completely two solutions of the reactants over a period of ~$10^{-3}$ s; the flow of the reaction mixture can be arrested with the aid of a removable syringe and electromagnetic valves over a period of $(1-5) \times 10^{-3}$ s.[32] These values are much shorter than those which are really necessary when an NMR spectrometer is used as the recording device, for which the dead time is limited by the transport time, amounting usually to $(50-100) \times 10^{-3}$ s. The principal elements of the flow technique—the mixing chamber and the syringe system for the injection of reactants and the arrest of the flow—have been almost wholly taken from analogous studies employing IR, UV, and EPR spectroscopy.[33,34]

When NMR is used in the continuous flow method, the dead time can be shortened mainly by reducing the transport time $\tau_{tr}$, which can be achieved, according to Eqn.(1), either by increasing the flow rate or by reducing the distance between the mixing and recording points. However, the increase of flow rate entails the shortening of the residence time of the spin state in the region of the receiving coil and, according to Eqn.(3), the broadening of the spectral lines. The decrease of the distance between the reactant mixing point and the spectrum recording point is therefore the most suitable procedure for shortening the dead time. In the stopped flow method the use of high rates of transport (under the conditions of an effective arrest of the flow) does not introduce additional distortions into the NMR spectrum and the experimental dead time can be reduced to several milliseconds.[35]

Since there are two fundamentally different methods of recording NMR spectra—stationary and pulsed, it is useful to divide all the published communications concerning the application of NMR in the study of fast irreversible reactions into two groups and to consider for each examples of the practical employment of the continuous and stopped flow methods. Special mention should be made of the difference between the speeds at which information can be secured by the above two methods of NMR measurements. Thus usually 4–5 min is required to record a spectrum 10 p.p.m. wide in the stationary regime of the operation of the NMR spectrometer, while the counting of the free induction signals in the same spectral region under a pulsed regime takes only 4 s. From the point of view of speed, the continuous flow method is more suitable for stationary NMR spectroscopy despite the considerable consumption of the initial reactants, while the stopped flow method is more suitable for pulsed Fourier-transform NMR.

## III. STATIONARY NUCLEAR MAGNETIC RESONANCE

When stationary NMR is used, the following conditions governing the passage of resonance lines must be maintained:[36]

$$\frac{d\nu}{dt} \ll (\Delta\nu_{1/2})^2,$$

where $\Delta\nu_{1/2}$ is the spectral line half-width. The time taken to record a single NMR signal should then be ~2–3 s, which determines the minimum possible scanning period in the stopped flow method. An increase in the rate of scanning distorts the signal both due to transient processes and as a result of the progressive saturation of the spin system.[37] The stopped flow method is therefore convenient for the study of the kinetics of chemical reactions whose half-life is more than 5–10 s. Since only a very narrow section of the overall NMR spectrum of the reaction mixture is recorded in this instance, the stopped flow method yields very little information from the standpoint of the determination of the structure of the intermediates. Even for comparatively slow reactions ($t_{1/2} > 5$ s) one therefore as a rule records initially the total spectrum of the reaction mixture with the aid of the continuous flow method in which the signal intensities are independent of time. The structure of the intermediates and the reaction pathways are inferred from the interpretation of the resulting spectrum and the process kinetics are then studied by the stopped flow method.

The kinetic data for the lifespans of the shortest-lived intermediates ($t_{1/2} \cong 0.1-1$ s) can be obtained only by the continuous flow method involving the variation of two independent parameters which determine the transport time in Eqn.(1). For intermediate values of $t_{1/2}$, the time variation of the concentration is found from data obtained by both methods.

### 1. The Continuous Flow Method

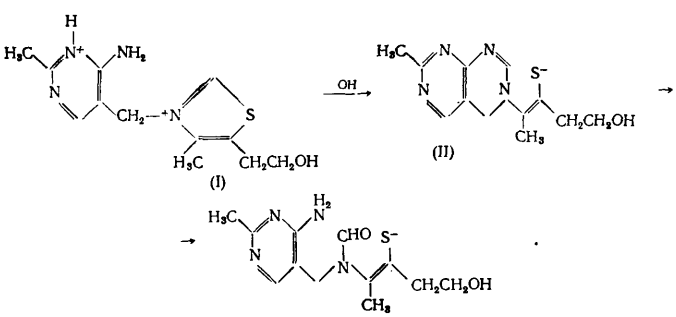
The possibility of using high resolution NMR in the study of fast irreversible reactions by the continuous flow method was first reported by Schaumberg,[38] who was not only the first to propose the preliminary magnetisation of the initial

reactants in the gap of the spectrometer magnet but also initiated a series of the most promising directions in the development of the technique and methods of NMR flow experiments, many of which have now been successfully realised. For example, the idea of using the saturation transfer effect[39] in the study of the mechanisms for irreversible chemical reactions whose half-life is comparable to the spin–lattice relaxation time is due to him. This method is based on the transfer in the course of reaction of the magnetisation defect of one or several nuclear spins; this magnetisation defect arises as a result of the inversion or saturation of the equilibrium magnetisation in the spin system of one of the reactants directed before mixing.

The experimental realisation of this method with the aid of a stationary spectrometer in the broad-band version as a method of inverting the magnetisation of one of the reactants has been achieved by Fife et al.[40], who used the rapid adiabatic passage through the resonance conditions by the specimen[41] in the non-uniform section of the magnetic field whose strength was $0.7H_0$. This method, called "electronic isotope substitution", might have permitted, in its selective version, the selective observation at any stage of the given reaction of the transformations occurring in a non-equilibrium reaction mixture. However, the creation of selective magnetisation defects in a flowing liquid must take place in the uniform section of a magnetic field $H_0$ and, owing to the finite residence time of the spin system in this region, in the continuous flow method this entails the overcoming of a series of technical problems,[24] which restricts the application of this method to stationary NMR. On the other hand, Fourier-transform NMR methods, which have appeared in recent years and which are based on multipulse trains,[42,43] are more convenient for the generation of a microwave frequency label in the spin system of one of the reactants and for the recording of its transfer in the course of an irreversible chemical reaction.[44–46]

The wide-scale experimental employment of NMR in a flowing liquid for the investigation of fast irreversible reactions began in connection with the discovery of the phenomenon of chemically induced nuclear polarisation (CINP) and the possibility of investigating radical reactions by NMR.[47] In 1967 Bargon et al.[19] first recorded in a flowing liquid the polarised signals of benzene—the diamagnetic product of a radical reaction initiated by photolysis. This so-called "Bargon" tube[46] played a major role in these experiments,[19,48,49] making it much simpler to carry them out because its use shortens the transport time (as a consequence of the use of a thin capilliary) and simplifies the removal of the spent reaction mixture (Fig. 2). The radical reaction is initiated outside the spectrometer magnet and the polarised products are then transferred via a connecting tube to the NMR sensor in order to record the spectrum.

A simpler modification of the Bargon tube has been used[51] to detect the unstable thiol form (II) formed in the reaction of the thiazole (I) with KOH:



A vacuum pump ensured the removal of the spent reaction mixture from the rotating tube at a flow rate of 3 ml $min^{-1}$. The authors[51] obtained the complete NMR spectra of the reaction mixture, corresponding to its composition 5 s after mixing the reactants.

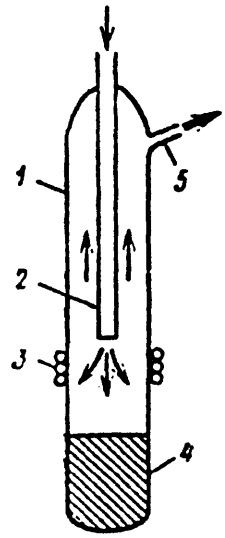
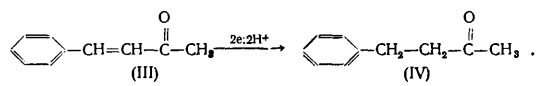



**Figure 2.** Bargon tube:[50] *1*) rotating bulb; *2*) capillary for the rapid injection of the reaction mixture into the recording region; *3*) receiving coil of spectrometer; *4*) Teflon insert for the optimisation of the recording volume; *5*) aperture for the removal of the reaction mixture.

An analogous technique has been used[20] in the study of the electrochemical reduction of the unsaturated ketone (III):



The NMR spectra of the electrolysis product (IV) were measured at a flow rate of 0.4 ml $min^{-1}$ and a current in the range 0–5 mA.

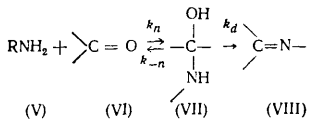
Lawler and Halfon[52] used a second additional magnet for the preliminary polarisation of the nuclei in the test system and investigated the dependence of the CINP effect on the field strength of this magnet in the photolysis of di-t-butyl ketone; the maximum flow rate did not exceed 4 ml $min^{-1}$.

The experimental dead time achieved with the aid of the Bargon tube was several seconds, which was quite sufficient for the solution of the problems formulated in the above investigations. A further shortening of the dead time within the framework of the given technique is difficult owing to the necessity for the effective preliminary polarisation of the n;uclei and the difficulty of ensuring the rotation of the specimen at high flow rates.[53] These disadvantages have been eliminated in a study,[54] where, by abandoning the rotation of the specimen, it was possible to raise the flow rate of the reaction mixture to 60 ml $min^{-1}$#.[55] The equilibrium magnetisation was attained with the initial

#A further increase of the flow rate led to excessive (more than 5 Hz) broadening of the lines in the NMR spectrum.[54]

reactants flowing through two polarisation coils placed between the sensor and the pole tips of the spectrometer magnet; the reactants were mixed in a Teflon mixer, which was fixed over the inlet opening to the sensor and was rigidly connected to the recording channel. Two pairs of tangentially disposed inlet openings ($d_{in}$ = 0.36 mm) into the high pressure mixing chamber ensured the rapid and effective mixing of the reactants. In order to reduce the time required for the transport from the sensor, the device ensuring the rotation of the specimen under the standard conditions of the operation of the spectrometer was removed and the mixing chamber was thereby brought as close as possible to the recording point; in addition, the diameter of the recording channel outside the region of the receiving coils was reduced to 2.5 mm.

With the aid of this technique, Fife, Cocivera, and co-workers carried out and published about 30 studies, some of which have been discussed in a review.[56] The studies[57-63] of the mechanisms of the reactions involving the nucleophilic addition of nitrogen-containing bases (V) to the carbonyl group (VI) are based on the measurement of strong-field NMR spectra of the signals due to the methyl protons of the aminocarbinol fragment (VII):



(V) (VI) (VII) (VIII)

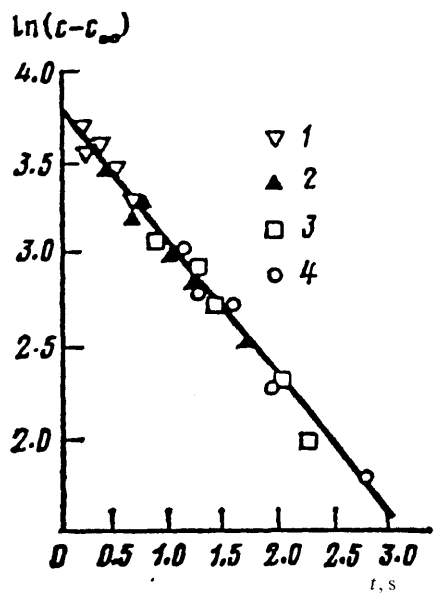
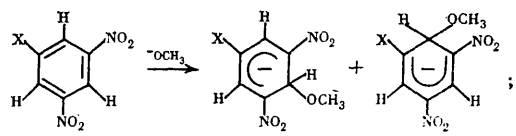



**Figure 3.** Dependence of $\ln(c - c_\infty)$ on $t$, where $c$ is the concentration of compound (X); distance between the mixing and recording points (cm):[65] *1*) 4; *2*) 5; 3) 6; 4) 7.

The authors were able to observe individual signals due to form (VII) only in the study of the interacton of acetaldehyde with hydroxylamine.[61] Owing to the reversibility of the first stage, in the remaining cases the spectrum showed the signals of the corresponding protons of the initial form (VI) and the intermediate form (VII) averaged by the rapid exchange (VI) ⇌ (VII). A standard approach, based on the determination of the half-width of the line averaged by the rapid exchange and of its position in the spectrum, was used to estimate the rate constants for the forward and reverse reactions ($k_n$ and $k_{-n}$) in these cases.

Thus the application of the continuous flow method extended the applicability of dynamic NMR in the study of the reversible stages of non-equilibrium reactions. The additional broadening of the lines associated with the movement of the reaction mixture [see Eqn.(3)] in these experiments was taken into account by introducing into the reaction mixture inert line form standards—t-butyl-alcohol[58] or methyl alcohol.[57] The position of the line of the standard molecule in the spectrum served simultaneously as the reference point for the reckoning of the chemical shift. The absorption lines of the solvents $H_2O$, $CH_3OH$, and DMSO were used as stabilisation signals. In the study of Cocivera and Effio,[57] the mixing chamber with six inlet openings was placed within the tube (5 mm) in the immediate vicinity of the receiving coil of the spectrometer sensor, which made it possible to reduce by a factor of 3 the transport time without increasing the flow rate of the reaction mixture.

Other studies by the same investigators[55,64,65] were devoted to the nucleophilic aromatic substitution reactions. The method is based on the direct recording of the thermodynamically unstable product (X) and the experimental determination of its lifespan as a function of the structural characteristics of the substrate (IX):

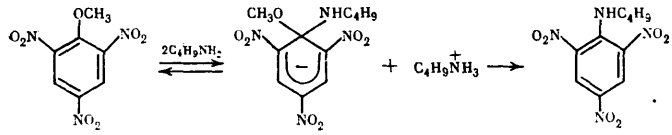


(IX) (X) (XI)

X = CN, $CF_3$, $COOCH_3$, $COOCH_2CH_3$, $COOCH(CH_3)_2$, $COOC(CH_3)_3$.

Fife et al.[65] demonstrated the possibility of using the continuous flow method to determine the kinetic parameters of fast reactions by varying the flow rate or the distance between the mixing and recording points. Such measurements yield a set of overlapping results for different experiments (Fig. 3) and ensure the determination of reliable kinetic data.

Yet another important methodological feature of the studies by this group of workers was the involvement in NMR flow measurements of the procedure for the study of the irreversible reactions in which the reaction mixture is cooled.[66-71] This makes it possible, on the one hand, to move the system to the range of reaction rates convenient for study and to detect in the reaction mixture the intermediates which are absent at room temperature and, on the other hand, it permits a wider employment of the more economical stopped flow method. The separate temperature control of the recording region and of the initial reactants has been employed in a number of studies.[61-66] The recording channel was cooled by means of a standard gas thermostatic control system, while the initial reactants were cooled by passing them through a liquid thermostat.[66-74] The temperature of the reaction mixture was measured before and after the experiment with the aid of methanol as the NMR temperature standard. Such a cooling system permits a reduction of the temperature to −40 °C and a qualitative study of the composition of the reaction mixture under these conditions Thus the interaction of 2,4,6-trinitroanisole (XII) with n-butylamine has been investigated:[66-68]



(XII) (XIII)

At −40 °C the maximum concentration of the intermediate (XIII) is observed 1 s after the start of the reaction (Fig. 4).

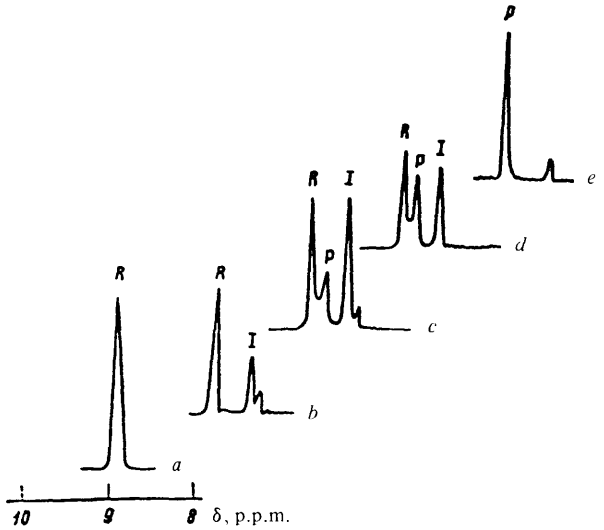



**Figure 4.** Section of the $^1$H NMR spectrum of a mixture of 2,4,6-trinitroanisole (XII) with n-butylamine at −40 °C obtained by the continuous flow method before (*a*) and at different times after mixing the reactants [*b*) 0.44 s; *c*) 0.98 s; *d*) 1.5 s; *e*) 30 s];[67] *R*, *I* and *P* are the absorption signals of the ring protons of the initial reactant, the intermediate, and the reaction product respectively.

The main disadvantage of the cooling method considered is the separate thermostatic control and the separate measurement of the temperatures of the initial reactants and of the recording region and also the existence under these conditions of a non-thermostatted section, including the mixing chamber. The above disadvantages§ can lead to considerable errors in the determination of the exact reaction temperature and to technical difficulties in its measurement during the flow experiment. Ultimately an appreciable scatter and poor reproducibility of the kinetic parameters of the reaction are observed.

§ Account should also be taken of the contribution to the error of the kinetic results introduced by the temperature gradient along the length of the recording channel, which is characteristic of the usual procedure for NMR measurements over a wide range of temperatures. The temperature drop along the length of the recording section of the reaction mixture can reach several degrees.[75]

It is known that the best results can be obtained when the entire measuring cell and the components of the flow system are simultaneously temperature-controlled in a liquid thermostat.[76] However, in the case of NMR the measuring cell is the sensor whose standard design precludes this procedure for the thermostatting of the flowing specimen. The above problem has been solved with the aid of a closed liquid thermostatic system[77,78] for the entire flow apparatus, which made it possible not only to improve greatly the quality of the thermostatic control of the flowing specimen and the accuracy of the determination of the temperature in the course of the reaction but also to eliminate the need for the employment of secondary NMR temperature standards.[79,80]

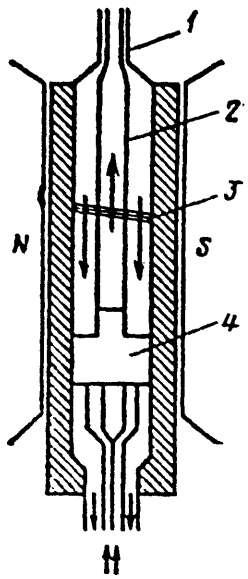



**Figure 5.** Liquid type thermostatic system in NMR flow experiments:[79] *1*) external circuit of the cryostat; *2*) recording channel; *3*) receiving coil of spectrometer; *4*) mixing chamber.

In the working regime two opposed streams are generated in the region of the receiving coil (Fig. 5): the stream of the reaction mixture within tube *2* which is 5 mm in diameter and the stream of the thermostatting liquid in the cylinder with an annular cross-section formed by the coaxially arranged glass tubes 12 and 5 mm in diameter. The mixing chamber *4*, located within the NMR sensor in direct vicinity to the receiving coil *3*, consists of a truncated cylinder and does not interfere with the circulation of the thermostatting stream. The disposition of all the elements of the flow system, including the initial reactants, within the outer circuit *1* of the cryostat ensures a high accuracy of the thermostatic control of the reaction mixture (±0.1 °C) in the temperature range from −40° to +60 °C. The influence of the absorption signals of the thermostatting liquid ($H_2O$, $CH_3OH$) on the spectrum of the reaction mixture is weakened owing to its incomplete magnetisation in the magnet gap[24] and the broadening associated with the decrease of its effective spin–lattice relaxation time $T_2^*$ [see Eqn. (3)]. This influence can be fully eliminated, for example, by introducing

paramagnetic additives.[28] The liquid thermostatic system for the flow apparatus was used in the study of the mechanism of the reactions of 1,3-diketones with hydrazines[81-83] and demonstrated the high reproducibility of the results of the kinetic measurements.

### 2. The Stopped Flow Method

The determination of data on the structures of the intermediates in irreversible chemical reactions by the continuous flow method is the first stage in the study of their mechanisms. The next stage consists of the study of the kinetics of the interconversions of the intermediates. If their half-lives are not less than 5 s, then kinetic data can be obtained with the aid of the stopped flow method by the rapid scanning of the selected section of the spectrum immediately after arresting the flow of the reaction mixture.

In order to achieve the rapid arrest of the flow in the stopped flow method, one usually employs a system with a third receiving syringe (Fig. 6). A microswitch ensures the disconnection of the reversible motor which moves the plungers of the supplying syringes. The time taken to arrest the flow by this method is usually ~1 s and permits the first recording to be made 2–3 s after the start of the reaction. The position of the microswitch can be varied within specific intervals within the limits of the amplitude of the movement of the plunger of the receiving syringe, which enables one to carry out repeated kinetic measurements under identical conditions.

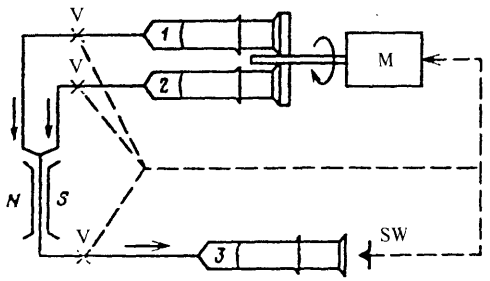
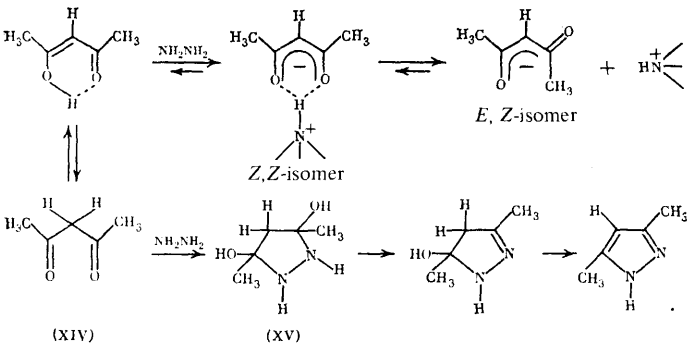



**Figure 6.** Schematic illustration of the apparatus for the stopped flow method: *1*) and *2*) supplying syringes; *3*) receiving syringe; SW = microswitch; V = electromagnetic valves; M = reversible motor.

The concentrations are usually determined from the integral[81-83] or peak[57-63] intensities of the corresponding signals in the NMR spectra. In carrying out the measurements, one must take into account the possibility of a synchronous increase of the intensities of all the signals during the reaction owing to the time variation of the dielectric constant of the reaction mixture.¶ The influence of this effect can be eliminated either by adding an inert signal intensity standard to the reaction mixture[58] or by calculating the relative signal intensities of all the components of the reaction mixture at each instant.[82,83]

The technique used in the cooling and thermostatting of the reaction mixture in the stopped flow method does not differ fundamentally in any way from that described for the continuous flow method.[67,79] The factors limiting the low-temperature measurements may be only the high freezing point of the solvent and the poor solubility of the individual components of the reaction mixture. The low temperature in the stopped flow method has been used[82] to demonstrate the higher reactivity of the keto-form of acetylacetone (XIV) compared with the enolic form in the reaction with hydrazine:




In methanol at −70 °C the attainment of the keto–enol equilibrium for acetylacetone is greatly retarded and the rapid formation of the dihydroxypyrazolidine intermediate (XV) from the keto-form can be observed immediately after mixing with hydrazine, while the enol form participates in the establishment of equilibrium between the hydrazinium salt having the *Z*, *Z*-configuration and the free anion with the *E*, *Z*-configuration.

The examples of the use of stationary NMR spectroscopy for the study of irreversible reactions discussed above show that the dead time of 0.05 s attained in the continuous flow regime[70] is apparently close to the limit for this method of measurement and further development of these procedures will take place to an increasing extent as a result of the wide-scale application of low-temperature measurements. This will permit the measurement of the NMR spectra of unstable intermediates in rapid non-equilibrium reactions which are inaccessible to investigation at room temperature even by the stopped flow method and will lead to the wider use of the more economical stopped flow method for kinetic measurements.

## IV. PULSED FOURIER-TRANSFORM NUCLEAR MAGNETIC RESONANCE

The main advantage of the pulsed Fourier-transform NMR is the simultaneous interaction of the microwave frequency pulse with all the spins of the non-equivalent nuclei, which makes it possible to accumulate in the study of rapid non-equilibrium reactions the free induction signals (FIS) at each point on the kinetic plot and hence to reduce the concentrations of the initial reactants in measurements involving the $^{1}H$ nuclei and also leads to the prospect of being able to employ $^{31}P$, $^{27}Al$, $^{13}C$, etc. NMR in the study of the compositions of non-equilibrium reaction mixtures.

¶This leads to the breakdown of the orthogonality of the polarisation of the microwave frequency fields of the receiving and transmitting coils which entails the leakage of the power of the transmitter to the input device of the receiver and a change in the regime governing its operation and hence to an identical distortion of the absolute intensities of all the signals in the spectrum.

The principal limitation in the wide-scale use of pulsed NMR in the study of rapid reactions is determined by the data access time, which for a spectral width of 8 p.p.m. is ~4 s and actually determines the minimum time interval between the recordings of the spectra in kinetic measurements. The artificial decrease of this interval by reducing the number of memory cells leads to the corresponding impairment of the quality of the spectra[15] but does allow one to reduce the scanning period in the stopped flow method to 0.1–0.2 s.[84]

### 1. The Continuous Flow Method

A characteristic feature of the pulsed regime in the operation of spectrometers is the difficulty, in principle, of obtaining the FIS from the flowing liquid.[85] After the application of the microwave frequency pulse, the signal is weakened owing to the continuous removal at a rate $v$ of the "excited" volume of the reaction mixture from the receiving coil. The increase of the rate of decay of the transverse component of the magnetisation ($M_{xy}$) in the time region corresponds to the widening of the absorption signals in the spectral region. In the present case this broadening is a complex function of the flow rate $v$, because the intensity of the recorded FIS diminishes as $1/l^2$ with the distance $l$ between the receiving coil and the excited volume.[24]

This problem can apparently be partly solved by employing a sensor with the receiving and transmitting coils separated by a specific distance which depends on the rate $v$. In order to eliminate completely the influence of the flow of the specimen on the line width, it is necessary to remove the receiving circuit during the recording of the FIS along the $y$ axis at a rate $v$ in the same direction, which presents significant difficulties.

Virtually no studies involving the use of Fourier-transform spectrometers in the continuous flow method have been described in the literature. In order to maintain a high concentration of a cell suspension in a state of equilibrium in studies of unstable biological objects by $^{31}$P NMR, the suspension was supplied continuously into the measuring region. In the accumulation of the FIS the access time was in this case reduced artificially to 0.2 s, which made it possible to avoid the distortion of the spectrum for a flow rate of the specimen of 5–10 ml min$^{-1}$.

One should also note the publications which appeared recently concerning the use of a flow-type Fourier-transform NMR spectrometer as the detecting device in liquid chromatography.[88–92] In terms of the technical and methodological problems solved in the above studies, they are closely related to the problems considered in this Section.

The conditions in the recording of $^1$H NMR spectra in quantitative measurements with the aid of a flow-type Fourier-transform spectrometer operating under accumulation conditions have been examined.[88] It has been found that, in order to eliminate the influence of various apparatus distortions in quantitative NMR flow measurements, it is best to introduce an intensity standard. It can be introduced either into the solvent before the mixing of the reactants or into the reaction mixture via the mixing chamber immediately before the recording.

The effect of the nuclear relaxation time $T_1$ on the measured signal intensity ratios in the spectrum was examined in the same study. It is inconvenient to eliminate this effect by increasing the arrest time between the pulses owing to the increase of the overall duration of the experiment. The requirement for the complete restoration of the Boltzmann equilibrium in the spin system is therefore not usually met. The use of the Bloch equation for the description of the equilibrium component of the magnetisation after a series of pulses,[93] which is a complex function of the spin–lattice relaxation time $T_1$, greatly simplified the analysis of the expression for the spectral density. It was concluded[88] that, in NMR flow measurements with pulsed recording of the composition of the reaction mixture, the accuracy of the quantitative measurements increases with decrease of the recording volume and with increase of the flow rate. Fig.7 illustrates the dependence of the effective spin–lattice relaxation times $T_1^*$ on the residence time $\tau$ of the spins in the recording region [see Eqn.(2)]. Evidently the lower the value of $\tau$, the smaller the difference between the values of $T_1^*$ for nuclear spins with different natural spin–lattice relaxation times $T_1^i$. The decrease of the effective spin–lattice relaxation times $T_1^*$ with the simultaneous equalisation for different nuclei in a flowing specimen has been used recently to increase the relative sensitivity of the recording of slowly relaxing quaternary carbon atoms in $^{13}$C NMR spectra.[94]

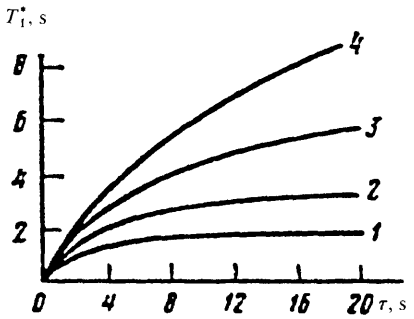



**Figure 7.** Dependence of $T_1^*$ on the residence time of the spin system in the recording region; natural spin–lattice relaxation times $T_1$(s):[88] *1*) 2; *2*) 4; *3*) 8; *4*) 16.

Thus the continuous flow method in the pulsed mode of operation of the spectrometer has no advantages over other NMR methods for the investigation of non-equilibrium reactions as regards the decrease of the experimental dead time, because it can be used only for very low flow rates of the reaction mixture ($\leq$1 ml min$^{-1}$) for which the distortions in the NMR spectrum due to the movement of the specimen can be neglected.

### 2. The Stopped Flow Method

An example of the employment of the pulsed Fourier-transform NMR for detection in the stopped flow method is provided by the studies of Grimaldy, Sykes, and co-workers who justified theoretically as early as 1972 [95] and later demonstrated in practice[96] the advantages of the pulsed methods for the study of rapid reactions compared with stationary NMR spectroscopy.[97,98] The simple application of the Fourier-transform NMR proposed by these workers consists in the successive recording of the NMR spectra of the non-equilibrium reaction mixture investigated within the limits of the inequality

$$n(\mathrm{AT} + \mathrm{TT} + \mathrm{PD}) \leqslant t_{1/2} \qquad (5)$$

where $n$ is the number of spectra recorded during the reaction time, AT the data access time, TT the time required for the Fourier transformation or for the transfer of the FIS to the memory device, and PD the delay period needed to restore the Boltzmann equilibrium ($AT + PD \geq 5T_1$). It follows from Eqn.(5) that, in order to increase $n$, it is necessary to reduce the times AT, TT, and PD. This is associated with additional distortions in the NMR spectrum. The PD time can be reduced to zero and for very short spin–lattice relaxation times ($T_1 \leq 0.1$ s) this does not introduce appreciable distortions into the final spectrum. The TT time can be reduced to 0.1 s by employing high-speed computers. The situation is different as regards the AT time, whose reduction to 0.1 s entails a broadening of the spectral lines to 5–10 Hz.[97]

Thus the method examined makes it possible to investigate reactions with half-lives up to 0.5 s and to reduce the dead time in experiments of this kind to 0.1 s. The method has been applied in a number of studies.[99–103] In an investigation of the kinetics of the base-catalysed deuterium exchange reaction between [$D_4$] methanol and the nitromethane anion (XVI), i.e.

$$CH_3NO_2 + [OCD_3]^- \xrightarrow{\text{fast}} [CH_2NO_2]^-,$$
$$[CH_2NO_2]^- + 2CD_3OD \xrightarrow{\text{slow}} [CD_2NO_2]^- + 2CD_3OH,$$
(XVI)

its slow second stage was recorded using pulsed NMR;[100] the microwave frequency pulses were repeated at 1.1 s intervals (Fig. 8). In order to increase the speed of recording, a spectral width of 1.2 kHz was used; time taken to transfer each FIS to the disc memory was 0.03 s.

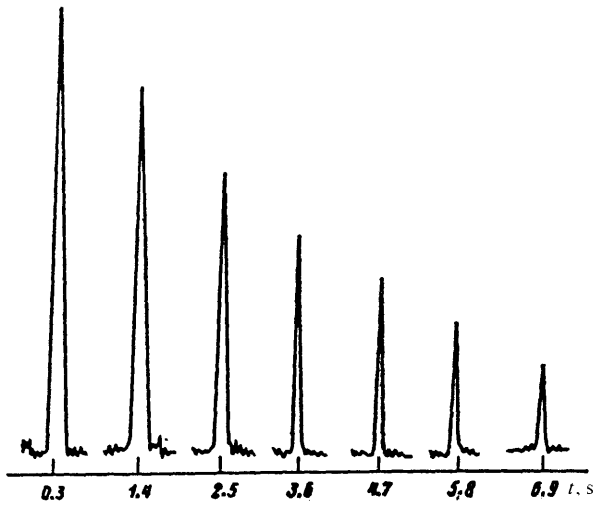



**Figure 8.** Decrease of the intensity of the signal of the nitromethane anion (XVI) ($\delta$ = 5.74 p.p.m.) during deuterium exchange with [$D_4$]methanol at 295 K.[100]

Another example of the effective use of this technique is provided by a study[102] of the hydrolysis of aluminium(III) by the method involving the $^{27}Al$ NMR of the reaction mixture; a single line is then present in the spectrum, which greatly facilitates the task of increasing the speed of recording such a spectrum. This enabled the authors[102] not only to obtain 20 points on the kinetic curve during 30 s but also to accumulate 20 FIS per second for each point.

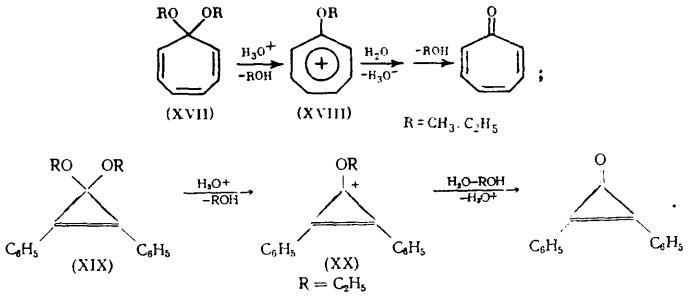
The question of the possibility of accumulating FIS in kinetic measurements has been examined in two investigations[95,105] and it has been concluded that the accumulation of several FIS at a single time point is legitimate only in the study of reactions proceeding in accordance with a first-order kinetic equation For reactions of higher order, the data must be accessed without accumulation. This problem plays a significant role in the employment of Fourier-transform $^{13}C$ NMR for kinetic measurements.[106–109] The difficulty of the quantitative analysis based on $^{13}C$ NMR spectra is associated with the influence of the spin–lattice relaxation time $T_1$ and the nuclear Overhauser effect on the peak intensities of the lines. In order to eliminate these influences on the recorded $^{13}C$ NMR spectrum of the non-equilibrium reaction mixture, it has been suggested[109] that longer delays be employed between the microwave pulses and that specific relaxation additives be introduced to shorten the time $T_1$, while in another study[108] the possibility of using special pulse trains for the same purpose has been discussed. However, as a rule, these procedures reduce the signal to noise ratio. For this reason, the differences between the spin–lattice relaxation times and Overhauser coefficients for individual atoms are usually ignored and the changes in signal intensities during the reaction are estimated with the aid of an intensity standard introduced into the reaction mixture.[106]

The technique used to mix the reactants in pulsed NMR flow methods differs little from that in the analogous devices employed in stationary NMR.[110,111] The synchronisation of the instant at which the microwave frequency pulse is triggered and the instant when the reaction mixture is transferred from the mixing chamber to the recording point requires special attention in the stopped flow method. A modern pulse Fourier-transform NMR spectrometer, which is equipped with a minicomputer, makes it possible to achieve readily not only the synchronisation of the start of the experiment but also one can program the entire experimental procedure.[13,84,99–104,110,112,113]

In order to shorten the dead time and to achieve the rapid arrest of the flow of the reaction mixture, various piston devices have been used.[84,99–103,110,113] In the first instant, local inhomogeneities in the composition of the reaction mixture can arise in the region of the receiving coil and can lead to additional broadening of the spectral lines in the first spectrum. Provision must be made for delays of 0.1 to 0.2 s to eliminate this effect before the first pulse of the kinetic series.

We believe that in many respects the apparatus and experimental methods proposed by McGarrity and co-workers[84,110] are optimal. By combining the mixing and recording points into one and using a novel mixing device, the authors[84] were able to achieve a reduction of the dead time to 0.04 s with effective stirring of the initial reactants directly in the rotating tube (Fig. 9). The preliminary polarisation of the initial reactants, one of which is in the tube and the other in the supplying capillary, is achieved naturally in the gap of the NMR spectrometer magnet. The problem of the temperature control of the recording region is solved simultaneously, which makes it possible to increase appreciably the accuracy of the kinetic measurements in conjunction with high reproducibility of the experimental conditions. To demonstrate the possibilities of this method, the authors repeated the study of the reaction of methylamine with trinitroanisole, which had been carried out earlier with the aid of stationary NMR in a flowing liquid.[67] The results and conclusions reached in this comparative investigation agreed fully with the available data, but the amount of initial

reactants consumed for this purpose was smaller by 2–3 orders of magnitude. Another example of the employment of this technique† is the direct detection of the unstable oxocarbonium ions (XVIII) and (XX) formed in the acid hydrolysis of the corresponding ketals (XVII) and (XIX):



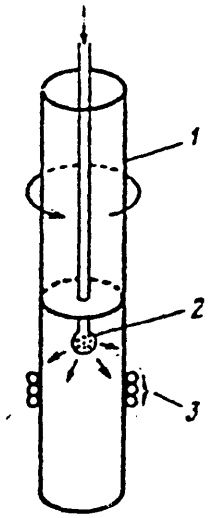




**Figure 9.** Apparatus for the rapid mixing of the initial reactants proposed by McGarrity et al.[84]: *1*) rotating bulb 5 mm in diameter; *2*) mixing device; *3*) recording region.

The tropylium ion (XVIII) proved to be sufficiently stable to detect it in an aqueous medium. On the other hand, the measurement of the $^1H$ NMR spectrum of the less stable intermediate (XX) required the use of the 1:1 $D_2O$–$(CD_3)_2CO$ mixed solvent; the lifespan of the intermediate in the reaction mixture was then 0.4 s.

The possibilities of the "rapid injection" method in securing quantitative kinetic information have been demonstrated[84] in the determination of the rate of hydrolysis of trimethyloxonium tetrafluoroborate (XXI):

$$\underset{\text{(XXI)}}{(CH_3)_3O^+BF_4^-} + 2H_2O \xrightarrow{k} CH_3OH + (CH_3)_2O + H_3O^+ + BF_4^- .$$

The kinetic relation (6) was obtained[84] on the basis of six kinetic experiments in each of which eight spectra were measured (Fig. 10):

$$\ln\left(\frac{[XXI]_t}{([XXI]+[CH_3OH])_t}\cdot\frac{([XXI]+[CH_3OH])_{t_0}}{[XXI]_{t_0}}\right) = -k(t-t_0) . \quad (6)$$

The instant when the first spectrum was recorded in each of the six kinetic experiments was adopted as the initial time $t_0$ in Eqn.(6). If the instant of mixing of the reactants were adopted as $t_0$, then, although the slope of each of the kinetic curves would be unaltered, the scatter of the points around the resulting straight line would depend on the efficiency of the mixing of the reactants in each experiment. As a result of the above choice of the time $t_0$ and the adjustment for consistency of the integral intensities of all the components of the reaction mixture at each instant, the error of the determination of the hydrolysis rate constant was less than 1%. Thus the above example shows that NMR can be used successfully for exact kinetic measurements.

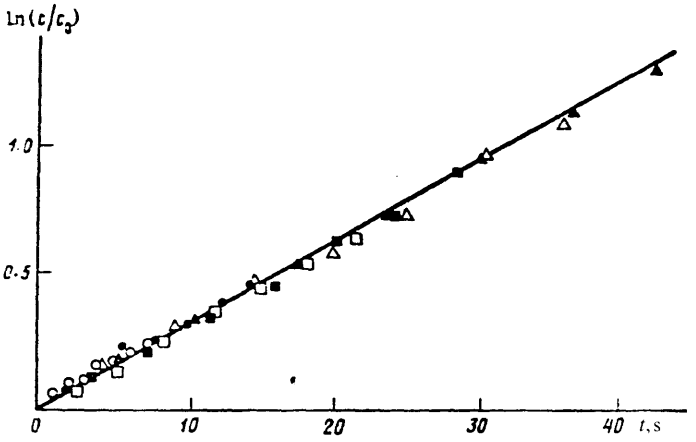
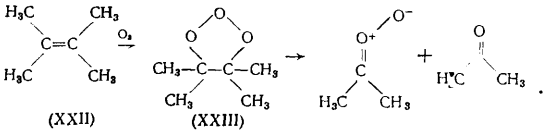



**Figure 10.** Kinetics of the hydrolysis of compound (XXI) in the 16:1 $D_2O$–[$D_3$]nitromethane mixed solvent at 23.4 °C; the points obtained in each of six independent measurements are designated by different symbols.[84]

The stability of the unstable intermediates in the reaction of tetramethylethylene (XXII) with ozone in [$D_2$]dichloromethane has been investigated by the rapid injection method:[110]




The use of low temperatures with a simultaneous reduction of the dead time of the kinetic measurements to 0.02 s and of the data access time to 0.1 s enabled the authors[110] to obtain half-reaction times of 4,4,5,5-tetramethyl-1,2,3-trioxolan (XXIII) in the temperature range from −80° to −100 °C and to estimate the thermodynamic parameters of its decomposition reaction. Even at −80 °C, where the half-reaction time is only 0.15 s, 11 spectra of the reaction mixture can be obtained for the construction of the kinetic curve. The error of the determination of $t_{1/2}$ does not then exceed 10%. The decrease of the temperature to −100 °C and the corresponding increase of $t_{1/2}$ to 3.2 s make it possible to increase the data access time and 25 virtually undistorted

†The technique of the NMR flow measurements was called by the authors the "rapid injection" method.[84]

NMR spectra of the reaction mixture can be obtained during the kinetic experiment (the error of the determination of $t_{1/2}$ at −100 °C is less than 2%).

The above study[110] was carried out on a spectrometer with a working frequency of 360 MHz and a superconducting magnet, which enabled the authors to reduce greatly the concentration of the initial reactants and to obtain qualitative $^1$H NMR spectra of 0.005 M solutions of the reaction mixture without the accumulation of the FIS.

Another promising aspect of studies of the kinetics of fast reactions by Fourier-transform NMR is the development of a dynamic resonance theory for non-equilibrium processes. In 1979 a group of investigators under the leadership of Ernst solved the problem of the influence of fast (comparable to the data time) non-equilibrium changes occurring in the spin system and the behaviour of the magnetisation vector.[113] They examined in a general form the non-normalised density operator $\sigma_j = [A_j]\rho_j$, where $\rho_j$ is the normalised density operator and $[A_j]$ the concentration of the molecules $A_j$, which depends on time under the conditions of an irreversible chemical reaction. Consequently the equation of motion for $\sigma_j$ is

$$\frac{d\sigma_j}{dt} = [A_j]\frac{d\rho_j}{dt} + \frac{d[A_j]}{dt}\rho_j .$$

Its solution for the line shape function $S_t$ has been obtained[113] for the simplest case of a first-order reaction. Analysis of the expression for $S_t$ permits the conclusion that the occurrence of rapid irreversible processes in the spin system does not lead to new spectral transitions compared with the equilibrium case. However, these processes are responsible for the broadening of the absorption lines of the initial reactants; the spectral lines of the product are not broadened, but they do undergo a phase distortion.

The fact that the amplitude and phase changes in the spectrum of the non-equilibrium mixture are analytically related to the reaction rate constant $k$ virtually leads to a new application of pulsed Fourier-transform NMR—the study by the method involving the total line shape analysis of the kinetics of irreversible chemical reactions whose half-lives are comparable to the data access time.

An an example, Fig. 11 illustrates the theoretical variation of the spectrum for the simplest case of a single-stage transition in a one–spin system $A \overset{k}{\rightarrow} B$ as a function of the rate constant $k$. The greatest changes in the spectrum of a non-equilibrium reaction mixture take place for comparable values of $k$ and of the difference between the chemical shifts of the initial reactant and the final product, while the character of the phase distortions of the line shape for the product is determined by the relative positions of the absorption signals for the initial and final states. Consequently the sign of the phase distortions of the NMR signal of the product is a criterion of the region in which the corresponding signal of the initial reactant is located relative to it.

Fig. 12 presents the theoretical spectra for a one-stage reaction of a two-spin system, $AB \overset{k}{\rightarrow} CD$, for different values of the rate constant $k$. These spectra were constructed subject to the following condition: as a result of the reaction, A is converted into C and B is converted into D; $\nu_A > \nu_C$ and $\nu_B < \nu_D$ and the phase distortions therefore have the opposite signs.

To demonstrate the possibilities of this new kinetic method, its authors selected the base hydrolysis of methyl formate (XXIV):

$$\underset{\text{(XXIV)}}{HCOOCH_3} + Na^+OD^- \xrightarrow[D_2O]{k_2} HCOO^-Na^+ + CH_3OD .$$

In the presence of an excess of NaOD, this reaction proceeds in accordance with a pseudofirstorder equation and the second-order reaction rate constant $k_2$ can be obtained from the expression $k_1 = k_2[O\bar{D}]$. The kinetic isotope effect, obtained from a comparison of the experimental and theoretical spectra of the reaction mixture (a mixture of a 0.15 M solution of lithium formate and a 0.63 M solution of NaOD) in $H_2O$ and $D_2O$, is

$$k_2(H_2O)/k_2(D_2O) = 0.64 \pm 0.08 .$$

This value is comparable to the familiar literature data (0.75).[114] The dead time in these measurements was $(3-5) \times 10^{-3}$ s and the number of repetitions of the experiments in order to accumulate the FIS ranged from

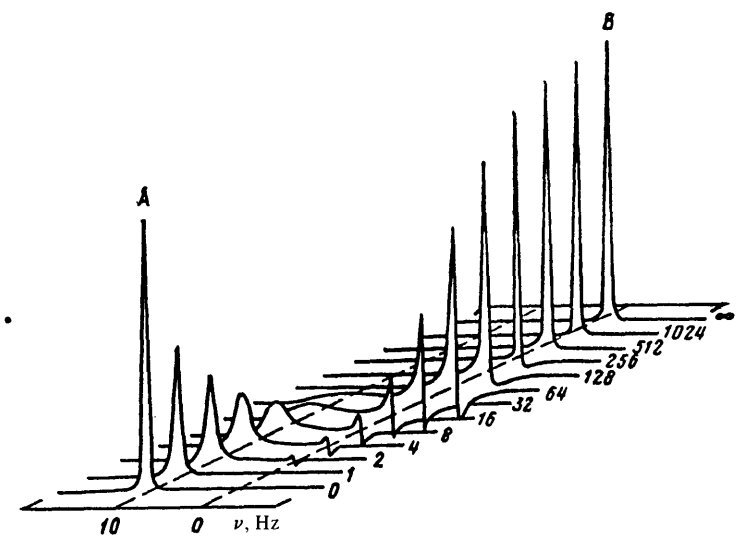



**Figure 11.** Theoretical dependence of the line shape for a single-stage reaction of a one-spin system for different rate constants $k$;[113] the numerals opposite each spectrum denote the values of $k$ (Hz) ($\nu_A - \nu_B = 10$ Hz).

40 to 100. In order to reduce $\tau_0$, the volume of the recording medium was artificially diminished and in the determination of the temperature of the reaction mixture a correction, taking into account the temperature rise (it did not exceed 3 °C when the accuracy of the thermostatic control of the recording region was to within 1 °C), was applied.

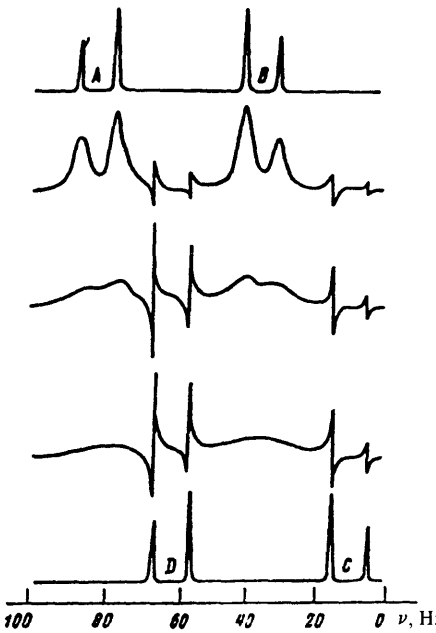



Figure 12. Theoretical variation of the line shape for a single-stage reaction of a two-spin system for different rate constants $k$(Hz):[113] *1*) 0; *2*) 10; *3*) 30; *4*) 50; *5*) ∞ ($\nu_A$ = 80 Hz, $\nu_B$ = 35 Hz, $\nu_C$ = 10 Hz, $\nu_D$ = 60 Hz, $J_{AB}$ = 10 Hz, $J_{CD}$ = 10 Hz).

The use of the method involving the total analysis of the line shape in order to obtain kinetic data for non-equilibrium chemical reactions[113] is so far limited to first-order reactions for which it is possible to obtain explicit analytical relations between the line shape in the NMR spectrum and the rate constant $k$. For higher-order reactions, numerical integration is required, which greatly complicates the construction and interpretation of the theoretical spectra.

The Fourier-transform NMR has been used for the first time[44–46] to study non-equilibrium chemical reactions with the aid of the saturation transfer effect, which has been applied previously only in the study of equilibrium reactions.[5,39] This selective magnetisation defect, which the authors[44–46] called the "microwave frequency label", is generated with the aid of a homonuclear decoupler by saturating the signals of specific atoms in the initial reactant directly before measuring the $^1$H NMR spectrum of the reaction mixture. The method involving the microwave probing of chemical reactions under specific conditions[46] makes it possible to trace, by employing NMR spectra, the path followed by the labelled atom in the course of the reversible reaction from the initial reactant to the product. The transfer of the label can be recorded by comparing the signal of intensities in the NMR spectra obtained with saturation and in the absence of saturation of specific signals from the initial reactant.

Fig. 13 illustrates the $^1$H NMR spectra of the reaction mixture of allyltriethylstannane (XXV) and bromotrichloromethane obtained under different conditions in the course of the photochemical reaction

$$(C_2H_5)_3Sn\overset{1}{C}H_2—\overset{2}{C}H=\overset{3}{C}H_2 + BrCCl_3 \xrightarrow{h\nu}$$

(XXV)

$$\xrightarrow{h\nu} CCl_3\overset{1'}{C}H_2—\overset{2'}{C}H=\overset{3'}{C}H_2 + (C_2H_5)_3SnBr\,.$$

(XXVI)

[the numerals 1, 2, 3, and 1′, 2′, and 3′ denote isotypical groups of atoms the reactant (XXV) and the product (XXVI), whose signals are indicated in the NMR spectra in Fig. 13*a*].

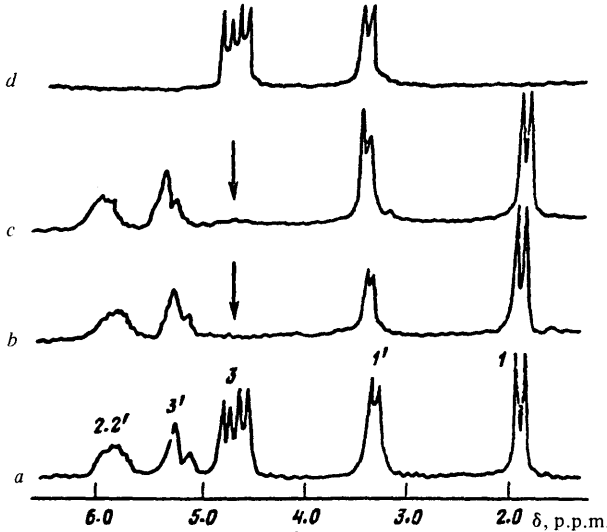



Figure 13. A section of the $^1$H NMR spectrum obtained in the course of the photochemical reaction of compound (XXV) with bromotrichloromethane in [$D_{12}$]cyclohexane under different conditions: *a*) reaction mixture without microwave frequency saturation of signals (the numerals denote the line assignment); *b*) and *c*) with saturation of the signals in the 3-position in compound (XXV) (the arrow indicates the position of the saturating field); spectra *b* and *c* were obtained with and without irradiation of the specimen by light respectively;[44] *d*) as for spectrum *b* but obtained with the aid of a selective pulse train[46] (evolution time ~1 s).

The fact that the saturation of signal 3 from the initial reactant (XXV) leads to a decrease (by 30–40%) of the intensity of signal 1′ from the product (XXVI) (Fig. 13*b*) compared with the intensity of this signal in the spectrum obtained without irradiating the specimen with light (Fig. 13*c*), while saturation of signal 1 from the reactant (XXV) entails a decrease of the intensity of signal 3′ from the product (XXVI) demonstrates unambiguously the occurrence of the 3 → 1′ and 1 → 3′ transitions in this reaction.[44,45]

The main deficiency of this method for the recording of the microwave frequency label is that the saturation transfer effect is observed against the background of the signal from the part of the product whose magnetisation has already returned to the state of equilibrium. In order to eliminate this disadvantage, an effective method involving the artificial isolation of the signals due to labelled atoms in the NMR spectrum of the reaction mixture has been proposed.[46]

This is achieved by the selective separation of the magnetisation vectors of the "labelled" and all the remaining atoms of the initial reactant during the preparatory period of the pulse train containing two in-phase microwave frequency pulses (broad-band and selective). Fig. 13*d* illustrates the spectrum of the reaction mixture obtained as a result of the effect of such a pulse sequence in the case of the selective isolation of signals associated with the generation of a microwave frequency label in the atomic group 3 of the initial reactant (XXV). The spectrum consists of only two signals (3 and 1'), which demonstrates the occurrence of the corresponding reaction transition.[46]

In connection with the employment of Fourier-transform NMR in the study of non-equilibrium reactions, it is essential to examine also the problems associated with the use for this purpose of NMR involving "rare" nuclei. Despite the difficulties due to the low sensitivity of these methods, $^{13}C$,[80,106,115–117] $^{31}P$,[86,87,118] and even $^{15}N$ [119] NMR has been used in recent years to obtain qualitative information about the structure of unstable intermediates in a whole series of chemical and biochemical reactions. Such investigations merit attention, because they provide an idea about the character of the experimental difficulties arising when they are carried out. In assessing the methodological advantages of these studies, it is necessary to take into account the fact that the very concept of a "fast reaction" has a different significance for each of the above nuclei#. In the determination of the experimental dead time $\tau_0$ in the stopped flow method, it is therefore necessary to take into account in addition the total FIS accumulation time in order to obtain an acceptable signal to noise ratio, which is to a first approximation§ inversely proportional to the square of the natural abundance of the isotope employed.

The frequent repetition of the entire procedure for the generation of the FIS in the non-equilibrium reaction mixture and for the accumulation of such signals must be regarded as the simplest and most effective method whereby the dead time in such experiments can be reduced,[113,120] which naturally requires an appropriate increase in the amount of the initial reactants. It is even more difficult to extract quantitative (or semiquantitative) kinetic information from NMR involving "rare" nuclei, because here one must take into account the influence of the relaxation effects on the peak intensities of the NMR signals. These problems have been discussed in detail in a number of studies[106,108,109,121] of the use of $^{13}C$ NMR for the recording of CINP effects. To save time, it is recommended that an external computer be used in kinetic measurements either for the simple storage of FIS corresponding to different time points on the same kinetic relation[101,110] or for their summation at a single time point for each of the frequently repeated kinetic experiments.[113,120]

#According to the definition given by Caldin,[22] the term "fast reaction" in relation to a given method of measurement should be understood as one which cannot be investigated under normal conditions and by means of a standard experimental technique.

§Here no account is taken of other parameters of the spin system and the NMR spectrometer which determine the resulting signal to noise ratio.

## V. CONCLUSION

The examples of the use of high-resolution NMR in the study of the mechanisms of fast irreversible reactions examined above indicate a vigorous development of mainly the flow methods and methods for the recording of CINP effects in which a non-equilibrium initial state is generated respectively as a result of the rapid mixing of the initial reactants and a photochemical reaction. The simple apparatus developed for these purposes, based on the use of NMR in a flowing liquid, makes it possible to obtain not only the spectral NMR characteristics of the relatively unstable intermediates with lifespans up to 0.02 s [110] but also quantitative data concerning the kinetics of their reactions. The relative error of the kinetic measurements can be reduced to 1% [84] and the chemical shift[14] or the spin–spin interaction constant[96] can serve as a time-dependent physical quantity together with the integral (or peak) signal intensity. Although kinetic data obtained with the aid of NMR are less accurate than the analogous results of the kinetic studies using the more sensitive UV, IR, and EPR spectroscopic methods, they can prove extremely useful in those cases where the intermediates do not contain chromophoric groups or unpaired electrons.

A characteristic feature of the development of NMR methods for the study of fast reactions is at the present time the tendency towards a wider employment of the stopped flow method with pulsed Fourier-transform recording of the spectra. This can be explained both by the economy of the method from the standpoint of the consumption of the reactants and the possibility of programming the experiment and by the increased sensitivity owing to the accumulation of the FIS, which permit, on the one hand, studies involving $^1H$ nuclei in more dilute solutions and, on the other, the use on a wider scale of measurements involving the $^{13}C$, $^{31}P$, $^{27}Al$, $^{15}N$, etc., nuclei. Fig. 14 presents the dead times $\tau_0$ attained with the aid of various $^1H$ NMR methods. It is noteworthy that $\tau_0 \cong (3-5) \times 10^{-3}$ s has been obtained by the Fourier-transform NMR under stopped flow conditions, such times being characteristic of the flow technique involving UV and IR spectroscopic analysis of the composition of the non-equilibrium reaction mixture, while the scope of the continuous flow method with stationary recording of the spectrum has been virtually exhausted and is restricted to $\tau_0 \cong 0.05$ s.

Another trend involves the use of methods with rapid NMR measurements at low temperatures. This permits a considerable extension of the range of irreversible reactions susceptible to study. Thus a decrease of the temperature of the reaction mixture to −90 °C expands the NMR time scale by approximately 8 orders of magnitude: by 4 orders of magnitude owing to the rapid measurement and by a further 4 orders of magnitude as a result of the decrease of temperature. The technical difficulties which arise in the development of the low-temperature NMR flow technique are associated primarily with the requirement for the effective temperature control of the measuring channel taking into account the possibility of the self-heating of the reaction mixture in the course of an exothermic reaction or heating due to the pulsed irradiation in the sensor of the Fourier-transform spectrometer.[77] These problems have been solved most successfully in the "rapid injection" method,[84,110] which permits kinetic measurements at temperatures up to −100 °C.

A study[122] involving the use of the NMR spectrometer as the recording device in a non-isothermal method[123] for the investigation of fast reactions is of interest from the standpoint of the employment of low temperatures and the economy in the consumption of the initial reactants. This method

consists in recording the changes in the NMR parameters of a non-equilibrium reaction mixture in the course of a linear temperature variation.[124] Analysis of this relation permits the calculation of the activation energy for first- or second-order reactions tending to equilibrium on the basis of a single kinetic experiment.

The extension of methods for the study of fast equilibrium reactions such as the total line shape analysis (TLSA) and the saturation transfer effect (STE) to the non-equilibrium case leads to new possibilities for the measurement of kinetic parameters and the study of mechanisms of irreversible reactions with half-lives comparable respectively to the data access time of the Fourier-transform spectrometer and the spin–lattice relaxation time of a selectively polarised nucleus.[45,46] The microwave frequency probing method has already found a practical application in the study of the mechanism of photochemical reactions.[44–46] However, its unique possibilities in meeting specific requirements[46] can be used in the study of a wider range of organic reactions.

The creation in the system of a non-equilibrium initial state with subsequent observation of its transition to the initial or new equilibrium state constitutes a general method for the investigation of both equilibrium and non-equilibrium chemical reactions.[125] For this reason, experimental methods and techniques for the NMR recording of fast irreversible transitions induced by chemical reactions, which have been examined in this review, can be useful in the study of both irreversible and irreversible chemical reactions in combination with other familiar methods for disturbing the equilibrium such as temperature,[126] or pressure jump[22] methods etc. The absence of NMR studies of this kind is associated in many respects with experimental difficulties in the creation of a sharp temperature or pressure drop in the standard NMR sensor. Nevertheless, it is to be expected that in the immediate future these relaxation methods will develop, for example, on the basis of sensors with wide temperature and pressure ranges, which have already been devised (for the solution of other problems).[127–131]

The problem of the low sensitivity of NMR involving "rare" nuclei, which prevents their wide-scale employment in the study of non-equilibrium reactions, has been partly solved with the aid of multipulse methods for the transfer of polarisation between atoms coupled by the spin–spin interaction which have been developed in recent years.[132] These methods for the artificial increase of the sensitivity and the corresponding shortening of the accumulation time of the NMR spectra involving "rare" nuclei have already found applications in the study of non-equilibrium biochemical reactions associated with the metabolism of living organisms.[133] The possibility of obtaining high-quality $^{31}P$,[135–137] $^{13}C$,[117,138] and $^{19}F$ [139] NMR spectra in soft tissues in the course of several minutes with the aid of surface coils[134] has given rise to wide possibilities for medical diagnostics with the aid of NMR and studies in this field merit separate consideration.

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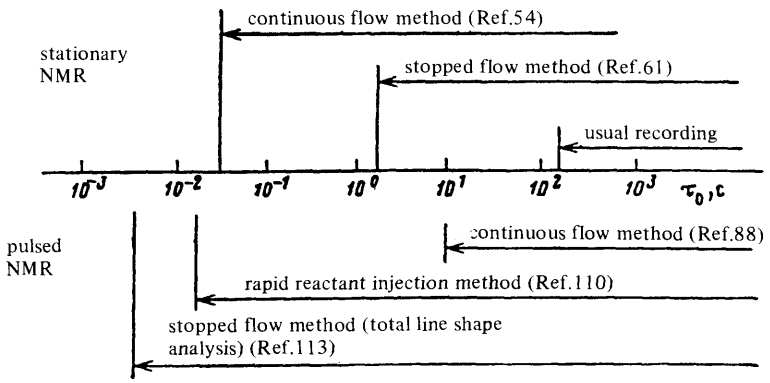




**Figure 14.** Experimental dead times $\tau_0$ in various NMR methods for the study of fast non-equilibrium chemical reactions.

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# Quantitative Estimation of the Electronic Effects of Substituents in Five-membered Nitrogen-containing Aromatic Heterocycles

V.A. Lopyrev, L.I. Larina, and T.I. Vakul'skaya

Data, characterising quantitatively the effect of substituents on the reactivity and physicochemical properties of five-membered nitrogen-containing heterocyclic compounds, which have accumulated in the literature during the last 15 years, are compiled in the review and discussed. The possibility of applying the Hammett and Jaffe equations in the determination of the direction of transmission of the electronic effects of substituents is analysed and the likely usefulness of this approach to the study of electronic influences by taking into account separately the inductive and resonance constants is demonstrated.
The bibliography includes 215 references.

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## I. INTRODUCTION

The current advances in theoretical organic chemistry are in many respects associated with the vigorous use of the principle of the linearity of free energies (LFE) in studies of a wide variety of reactions and physicochemical properties.

The Hammett equation makes it possible to obtain quantitative estimates of reaction rate and equilibrium constants and to predict many important physicochemical characteristics. It is used widely in the study of the relation between structure and biological activity. The greatest advances on these lines have been achieved in hydrocarbon systems.

During the last decade, the Hammett equation, which was initially proposed for simple aromatic systems, has undergone a series of modifications based on the separate allowance for the inductive and resonance effects of substituents and proved to be applicable to various heterocyclic compounds.[1-9] The application of correlation analysis to heterocycles is usually considered in terms of the following aspects:

(1) The heterocycle functions as a substituent and one estimates its influence on the reaction centre of the molecule.

(2) The heteroatom in heterocyclic compounds is regarded as a substituent introduced into the aromatic ring. Here one estimates its influence on the properties of the system.

(3) The heteroatom in the heterocyclic system behaves as the reaction centre.

(4) The heterocycle is regarded as a single system in which the substituent and the reaction centre interact.

Since the first three aspects have been dealt with in fair detail in other reviews,[5-7] we concentrated attention on the transmission properties of heterocyclic systems. Since the comprehensive review of Mamaev and Shkurko on the transmission of the effects of substituents in azines has been published recently,[9] we confined ourselves to the consideration of nitrogen-containing five-membered heterocycles and their condensed derivatives.

## II. PYRROLES, INDOLES, AND CARBAZOLES

The $pK_a$ for a large series of substituted pyrroles have been determined[10] by the method involving transmetallation in dimethyl sulphoxide and it was shown that the NH acidity of such derivatives is satisfactorily correlated with the inductive constants of the substituents:

$$pK_a = (23.4 \pm 0.1) - (17.4 \pm 0.5)\sum\sigma_I, \quad r = 0.994,\ S_0 = 0.37,\ n = 17. \qquad (1)$$

An equation was fitted in the same study to the available literature data for the acidity of the substituted pyrroles in water:

$$pK_a = (16.6 \pm 0.6) - (10.5 \pm 0.9)\sum\sigma_I, \quad r = 0.97,\ S_0 = 1.0,\ n = 11. \qquad (2)$$

The difference between the reaction constants in Eqns.(1) and (2) is due to the employment of different solvents in which the $pK_a$ scales differ significantly. Furthermore, the formation of complexes between pyrroles and dimethylformamide (DMF) was investigated in the same study by IR spectroscopy. The $\Delta\nu$ in the infrared spectra of the complexes are proportional to the square of the energy of the N–H...O hydrogen bond and are therefore a measure of the relative acidities of these compounds. The relative acidities determined in this way are also satisfactorily correlated with $\sigma_I$. The data described enabled the authors[10] to conclude that the influence of substituents on the NH acidity of pyrrole is determined mainly by the inductive effect. The complex formation method for the estimation of the NH acidities of a series of pyrroles in which the substituent is separated from the ring by the methylene bridge has also been used by Janda et al.[11] A satisfactory linear relation between the relative acidities and the inductive constants of substituents was obtained for a series of 2(5)-substituted pyrroles. These results have been partly surveyed in a review.[12]

However, the vibration frequencies of the free NH groups in 2-ethoxycarbonylpyrroles vary linearly with the $\sigma_p$ constants.[13] The study of the acidities of pyrrole-2-carboxylic and pyrrole-3-carboxylic acids[14,15] showed that the influence of the substituents is transmitted through the pyrrole ring via the same mechanism as for the phenylene fragment but with a somewhat higher intensity.

In a study of 2-phenylpyrroles containing different substituents in the *para*-position in the benzene ring[16] and of their *N*-vinyl derivatives,[17] it was observed that the $\delta(^{13}C)$

parameter for both the pyrrole ring and the β-atom of the vinyl group varies linearly with $\sigma_p$. It has been concluded[16] that the degree of conjugation of the phenylene fragment with the pyrrole ring is significantly greater than in the corresponding furan derivatives.

It has been shown that the $^1H$ and $^{13}C$ chemical shifts of the vinyl group in 2-alkyl- and 2,3-dialkyl-1-vinylpyrroles vary linearly with the steric constants of the subsituents.[18]

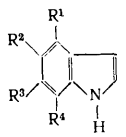
The ionisation energies, determined from the photoelectron spectra for two series of substituted pyrroles [5-R-3-ethoxycarbonyl-2,4-dimethylpyrroles (the α-series) and 4-R-2-ethoxycarbonyl-3,5-dimethylpyrroles (the β-series)][19] are linearly related to the $\sigma_m$, $\sigma_p$, and $\sigma_p^+$ constants ($r = 0.90$ to 0.97), the best correlation being obtained when $\sigma_p$ constants are used. It is of interest that the ionisation potentials for the α- and β-series of substituted pyrroles[19] are satisfactorily correlated ($r = 0.97-0.99$) with the $pK_a$ of 4-substituted[14,15] and 5-substituted[15] pyrrole -2-carboxylic acids.

A linear correlation between $E_{1/2}$ and the constant $\sigma_p^+$ has been noted in a study[20] of the electrochemical oxidation of 3,4,5-triphenyl-2-(4-R-phenyl)-, 3,4-diphenyl-2,5-di-(4-R-phenyl)-, 5-(4′-biphenylyl)-3,4-diphenyl-2-(4-R-phenyl)-, and 5-(2-naphthyl)-3,4-diphenyl-2-(4-R-phenyl)-pyrroles in DMF.

The theoretical reactivity indices have been calculated for a series of 2-monosubstituted pyrroles by the CNDO/2 method.[21] The correlations between the theoretical and experimental reactivity indices has led to the conclusion that the electronic effects of substituents are transmitted in different ways from the 2-position (correlation with $\sigma_p^+$ constants) and the 3-position (correlation with $\sigma_m^+$ constants) in the pyrrole ring.

There exist data showing that the rate constant for the decolorisation of benzene solutions of 2-aryl-3,4,5-tetraphenylpyrrolyl and 2-aryl-5-biphenylyl-3,4-diphenylpyrrolyl radicals are correlated with the overall σ constants.[22]

A quantitative estimation of the influence of the electronic effects of substituents on the acidity of indoles has been reported in only one communication:[23]



$$pK_a = 2.56 \sum\sigma - 2.55 \qquad r = 0.996, \; n = 9 \qquad (3)$$

The $\sigma_m$ constants for the $R^1$ and $R^4$ substituents and the $\sigma_p$ constants for the $R^2$ and $R^3$ substituents were used in the correlation in Eqn.(3).

The question of the electronic effects of the substituents in indole systems has been considered mainly from the standpoint of the determination of the path followed in the transition of these effects to the reaction centre. Jaffe[2] suggested that the equation

$$\lg K/K_0 = \rho_1\sigma_m + \rho_2\sigma_p \qquad (4)$$

be used to determine the direction of the transmission of the effects of substituents via carbon–carbon or nitrogen–carbon bonds. Having fitted this equation to the constants for the hydrolysis of indole-2-carboxylic acid esters and the ionisation constants of these acids, Jaffe failed to observe significant differences between $\rho_1$ and $\rho_2$. On this basis, he concluded that the transmission of the effects of substituents via the =CH– and –NH– groups is approximately the same.[2]

The study of the acidities of 5- and 6-substituted indole-3-carboxylic acids in aqueous ethanol showed[24] that the $pK_a$ are satisfactorily correlated with the $\sigma_m$ constants for the 5-substituted acids and the $\sigma_p$ constants for the 6-substituted acids. Hence it was concluded that the electronic effects of the substituents are transmitted mainly via the hydrocarbon chain and not via the "pyrrole" nitrogen atom. However, the same data were treated in terms of Eqn.(25) and the results ($\rho_1 = 0.31$ and $\rho_2 = 0.42$) indicate the approximately equal contributions of the methylidyne groups and the "pyrrole" nitrogen atom to the transmission of the electronic effects. Eqn.(4) was also used to analyse the rate constants for the reactions of indole-2-carboxylic and indole-3-carboxylic acids with diphenyldiazomethane[25] and fairly high correlation coefficients were observed (0.980 and 0.997 respectively).

Thus the conclusions reached on the basis of the Jaffe equation are to a considerable degree contradictory and, as will be shown below, the application of Eqn.(4) and other multiparameter relations for the estimation of the paths followed in the transmission of the electronic effects of substituents in heterocyclic systems, inccluding condensed heterocycles, is unjustified without the analysis of the relation between the arguments.

Somewhat later the question of the transmission of the influences of substituents through the indole ring was examined by Bowden and Parkin.[26] The authors investigated the ionisation of indole-2-carboxylic acids containing substituents in various positions in the ring and concluded that, in contrast to benzene compounds, the $pK_a$ for these acids cannot be expressed by any one correlation equation using different constants σ and the same value of ρ for all the positions in the indole ring. The correlation is satisfactory when the constants $\sigma_D$ are calculated for each position of the substituent within the framework of Dewar's theory or $\rho_1$ and $\rho_2$ are fitted in the Jaffe equation (4). The authors therefore suggest that independent constants be fitted for each position of the substituent. However, this procedure cannot be regarded as promising.

The equilibrium constants for the formation of enzyme–indole complexes are correlated with the Hammett σ constants and, when the reaction centre in indoles is the nitrogen atom, the constants $\sigma_p$ are used for 5-substituted derivatives and $\sigma_m$ for the 4- and 6-substituted derivatives.[27]

The basicities of a series of carbazoles have been determined by the method of standard indicators in 20% ethanol[28] and it was shown that they are related to the σ constants by the expression

$$pK_{BH^+} = (-5.18 \pm 0.95) - (5.01 \pm 0.26)\sigma, \; r = 0.993, \; n = 6$$

The $\sigma_m$ and $\sigma_p$ constants were used respectively for the substituents in the 2- and 3-positions.

In a study of the mechanism of the acid hydrolysis of 3,6-disubstituted 9-(1-alkoxyethyl)carbazoles[29] and 9-alkenylcarbazoles,[30] it was observed that the reaction rate constants are correlated more effectively with the Hammett constants than with the Brown $\sigma^+$ constants, which indicates the absence of a direct polar conjugation of the substituents in the carbazole ring with the carbonium centre in the transition state. The amount of double bond character between the carbazole ring and the reaction centre in the transition state is then smaller in the hydrolysis of 9-vinylcarbazoles than in the hydrolysis of 9-(1-alkoxyethyl)carbazoles ($\rho = -2.24$ and $-3.52$ respectively).

The results of a study of the reactivities of 6-substituted 3-aminocarbazoles have been published.[31] The authors determined the basicity constants for the above compounds and the rate constants for their reactions with picryl chloride and *p*-nitrobenzenesulphonyl bromide. Correlations were noted between the experimental data and the $\sigma^0$ constants ($r = 0.962-0.999$). The reactivities of carbazoles have been compared with those of the analogous substituted diphenylamine derivatives and it was noted that the reactivities of carbazoles are somewhat higher, while their sensitivity

to the electronic influences of the substituents is lower than that of diphenylamines. In this approach no account is taken of the specific features of the carbazole ring as a single aromatic system, which undoubtedly reduces the value of the conclusions reached in the above study.

A thorough investigation of the transmision of the effects of substituents through the carbazole ring in 3-substituted 9-methylcarbazoles has been undertaken by $^{13}C$ NMR.[32] The authors of this study carried out one-parameter correlations between the chemical shift of the carbon atoms in the carbazole ring and the Brown $\sigma_p$ and $\sigma_p^+$ constants as well as two-parameter correlations taking into account the $\sigma_I$ and $\sigma_R^0$ constants. The results led to the conclusion that there is a direct polar conjugation within the limits of a single phenylene fragment. An attempt was also made to estimate the direction of the transmission of the effects of substituents on the basis of the satisfactory correlations $\Delta\delta[C(6)]-\sigma_p$ and $\Delta\delta[C(7)]-\sigma_m$ ($r = 0.964$ and 0.941 respectively). The "dominant" diphenylamine direction (i.e. via the nitrogen atom) proposed by the authors[32] apparently does not altogether correspond to reality, because, as will be shown below, it is not legitimate to employ one-parameter correlations for the determination of the paths followed in the transmission of the effects of substituents in heterocyclic systems.

## III. PYRAZOLES AND INDAZOLES

A limited amount of data concerning the application of the LFE principle to pyrazoles and indazoles is available in the literature. The study of the basicities of 90 derivatives of pyrazole has shown[33] that the $pK_{BH^+}$ are correlated with the Hammett $\sigma_m$ constants. In a study of the electrochemical oxidation of pentacyanoferrate(II) complexes of pyrazole and indazole, an excellent correlation was observed ($r = 0.99$) between the oxidation potentials and the $pK_{BH^+}$ for the ligand.[34] Although direct correlations with the parameters of the substituents are not quoted, presumably (bearing in mind the study of Elguero et al.[33]) the oxidation potentials of the pentacyanoferrate(II) complexes of pyrazole also depend linearly on the $\sigma_m$ constants).

The equilibrium NH acidities of pyrazole derivatives (3,5-dimethylpyrazole, pyrazole, 4-chloro-3,5-dimethylpyrazole, and 4-bromopyrazole) are satisfactorily correlated with the sum of the $\sigma_m$ constants of the substituents regardless of their positions in the heterocycle.[35] However, the authors themselves recognised that one cannot infer that the relations obtained are general on the basis of the four available points.

In the course of the study of the kinetics of the hydrolysis of *N*-acylazoles, it has been shown that the rate constants for the hydrolysis of 4-substituted *N*-acylpyrazoles are correlated with the $\sigma_p$ parameters.[36] The reliability of this relation is difficult to assess, since the results of a statistical treatment are not quoted.

A study of the polarographic reduction of 3-aryl-1,2-dimethylpyrazolium perchlorates[37] has shown that the half-wave potentials for the two-electron transfer are satisfactorily correlated with the Hammett $\sigma$ constants of the substituents in the 1-position. Unfortunately, correlation equations are not quoted in the above study and the relations are presented in the form of a graphical plot without a due statistical treatment.

The $^{13}C$ NMR spectra of 3-substituted indazoles have been investigated[39] but no correlation has been observed between the chemical shifts and the parameters $\sigma_m$, $\sigma_p$, $\sigma_I$, and $\sigma_R$. When the parameters of Swain and Lupton[40] ($\mathcal{F}$, $\mathcal{R}$) were used, a correlation was observed only for $\delta[C(5)]$,[39] but the large errors in the coefficients of the correlation equation and the unsuccessful selection of the points preclude the estimation of the influence of the electronic effects of the substituents.

## IV. IMIDAZOLES

The influence of substituents on the acid–base properties of the imidazoles has been studied in fair detail.[41–52] The main contribution in this field is due to Charton,[7,41] who showed that the $pK_{BH^+}$ of substituted imidazoles are better correlated with the $\sigma_m$ or $\sigma_I$ constants than with the $\sigma p$ constants. For certain series, the data have been treated in terms of a two-parameter correlation equation using the $\sigma_I$ and $\sigma_R$ constants.[43] These data led to the conclusion that the employment of two-parameter correlations does not improve the regression parameters.[41] However, this conclusion cannot be regarded as reliable because both the number and the selected sets of points in the series do not satisfy the recommended requirements for two-parameter correlations.[48,53]

The basicities of 2-phenyl-substituted 4,5-diphenylimidazoles in acetonitrile have been investigated[47] and it was found that the correlation between the basicity constants and the $\sigma_p$ constants is excellent, while the correlation with the $\sigma^+$ constants is much worse. The same data have been treated in terms of a two-parameter equation using the $\sigma_I$ and $\sigma_R^+$ constants and in terms of the Yukawa–Tsumo equation:[47]

$$pK_{BH^+} = 12.72 + 1.974(\sigma^0 + 0.269\Delta\sigma_R^+),\ R = 0.998\ n = 6\ .$$

A decrease of the basicity of the imidazole ring was noted after the introduction of aryl substituents in the 1-position.[49] When the substituents are in the aromatic ring, satisfactory correlations are obtained when $\sigma$ constants are used ($r = 0.958$), electron-accepting substituents ($NO_2$ and $COCH_3$) deviating from the linear relation, which the authors explained by their polar conjugation with the reaction centre.

In a study of the basicity of nitroimidazoles, an attempt was made to introduce special $\sigma$ constants for compounds of this class.[50] However, it is not possible to assess the reliability and the results of the above study because the correlation equations themselves are not quoted.

The acid properties of imidazoles have been investigated.[34, 43,51] The equilibrium NH acidities of imidazoles and their derivatives[35] are satisfactorily described, like the acidities of pyrazoles, by a linear relation between the $pK_a$ and the sum of the $\sigma_m$ constants of the substituents regardless of the positions which they occupy in the heterocycle:

$$pK_a = 18.9 - 9.5\sum\sigma_m,\ S = 0.25,\ r = 0.9991,\ n = 5\ .$$

The authors believe that, since there are no $\pi$-acceptor groups other than the phenyl group among the substituents investigated, it is diffiult to judge to what extent the relation found is general.

The acidity constants of 4(5)-substituted imidazoles are described by the equation[43]

$$pK_a = 13.90 - 6.72\sigma_I - 2.77\sigma_R,\quad R = 0.988,\ n = 5\ .$$

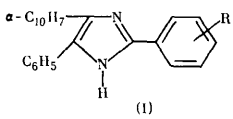
The limited set of substituents in this series (H, $C_6H_5$, CHO, $CONH_2$, $NO_2$) and the lack of electron-donating substituents lower the value of the above equation.

The acid dissociation constants of nitroimidazole have been determined recently[51] and it has been shown that the $pK_a$ for 2-substituted 4(5)-nitroimidazoles vary linearly with the $\sigma_m$ constants:

$$pK_a = 9.1625 - 8.8845\sigma_m.$$

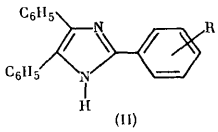
Similar relations have not been observed for 5(4)-substituted 4(5)-nitroimidazoles.[51]

The influence of the substituent in the arylene fragment on the acid properties in the series of imidazole derivatives (I)–(IV) has been investigated: [52]



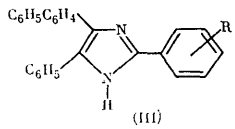
$\Delta\nu = 34\sigma + 221$, $r = 0.97$, $n = 7$ ;

(I)



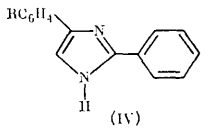
$\Delta\nu = 22\sigma + 215$, $r = 0.98$, $n = 10$ ;

(II)



$\Delta\nu = 15\sigma + 217$, $r = 0.96$, $n = 6$ ;

(III)



$\Delta\nu = 10\sigma + 210$, $n = 4$ .

(IV)

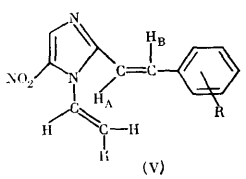
The authors explained the different sensitivities to electronic influences in the (I)–(IV) series by the effect of the direct polar conjugation between the substituents in the 2- and 4-positions in the imidazole ring. A deficiency of this treatment is that the differences between the steric effects of bulky subsituents in the 4- and 5-positions in the imidazole ring are excluded from consideration.

The heteroanalogues of triarylimidazoles have been investigated as inhibitors of the radical polymerisation of methyl methacrylate. [54] A linear relation has been observed between the logarithm of the inhibition factor and the Hammett $\sigma^+$ constants.

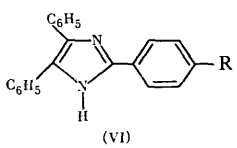
In a study of the photoelectron spectra of methylimidazole, it has been observed that the ionisation energies vary linearly with the basicity constants. [55] Since it is known that the latter are in their turn linearly related to the constants, [7,41] presumably their ionisation energies should also be correlated with these constants.

One-parameter correlations of the chemical shifts $\delta(^1H_A)$ with the $\sigma_R^0$ constants and two-parameter correlations of the chemical shifts with the $\sigma_I$ and $\sigma_R$ constants have been published for a series of substituted 5-nitro-2-styryl-1-vinylimidazoles (V). [56]

A correlation has been noted between the half-wave oxidation potentials of 2,4,5-triarylimidazoles (VI)–(VIII), [57,58] 2,4-diaryl-5-heterylimidazoles (IX), [59] and 4,5-diaryl-2-heterylimidazoles [59,50] and various constants. It is noteworthy that the potentials $E_{1/2}$ for the anions of the series (VI) depend on the $\sigma_p$ constants. [57]

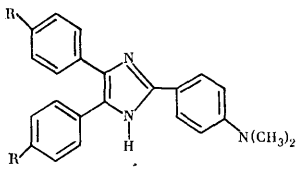


(V)



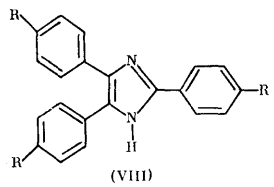
(VI)

R = $N(CH_3)_2$, $OCH_3$, $CH_3$, H, Cl, $NO_2$



(VII)

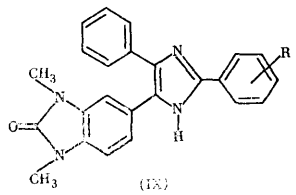
R = $N(CH_3)_2$, $OCH_3$, $CH_3$, H, Cl



(VIII)

R = $N(CH_3)_2$, $OCH_3$, $C_6H_5$, H, Cl

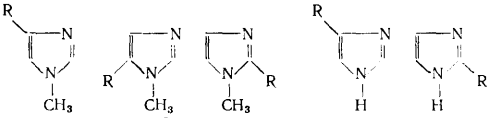
In the series (VI), 2-(*p*-nitrophenyl)-4,5-diphenylimidazole deviates from the correlation, which can be accounted for by the polar conjugation of the nitro-group with the reaction centre in the anion. The reaction constants for the series (VI) and (VII) are approximately equal ($\rho = 0.295$ and 0.284 respectively) and are smaller almost by a factor of 2 than for the series (VIII) ($\rho = 0.580$). [57] Unfortunately a statistical treatment of the correlations is not presented in the given communication. The $\sigma^+$ and $\sigma$ constants were used by Shishkin et al. [58] and Blokhin et al., [59] on the one hand, and Rozin et al., [60] on the other, respectively in the statistical treatment of the results of the polarographic oxidation of the structurally similar compounds (IX):



(IX)

The relatively low reaction constants show, according to the authors, that the half-wave potential is determined mainly by the dimethylbenzimdazolone substituent. [59] However, this conclusion is inconsistent with other data. [57] Satisfactory correlations have been obtained ($r = 0.949$) between the rate constants for the quaternisation of 1-arylimidazoles and the Hammett $\sigma$ constants of the substituents in the aryl fragment, although a low sensitivity of this reaction to electronic effects was noted. [49] A satisfactory correlation of the reaction rate constants for the azo-coupling of 2-substituted imidazoles and *p*-diazobenzenesulphonic acid with both $\sigma_m$ and $\sigma_p$ constants has been noted, [44] but, in view of the limited set of the substituents, the above relations cannot be treated as entirely reliable.

The influence of the electronic parameters of substituents on the solvolysis of *N*-acylimidazoles has been examined in several communications. [61–63] The rate constants for the acid [61] and base [62] hydrolysis of aroylimidazoles depend on the $\sigma$ constants of the substituents in the aroyl fragment. The rate constants for the solvolysis of 1-(1-methyl-2-imidazolyl)-ethyl *p*-nitrobenzoates have been measured and it has been shown that they are linearly related to the $\sigma_m^+$ constants for the 4-substituted derivatives and to the $\sigma_p^+$ constants for the 5-substituted derivatives. [63] The base-catalysed isotope exchange involving the substituted imidazoles (X)–(XIV) has been investigated. [64]

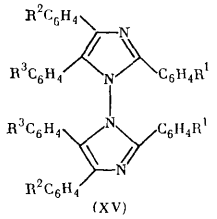


(X) (XI) (XII) (XIII) (XIV)

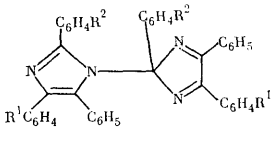
The set of substituents is the same in each case: $NO_2$, F, H, $CH_3$, and $CF_3$. The authors showed that the isotope exchange proceeds via two different mechanisms involving the intermediate formation of substrate anions or cations.

In the above study a significant difference between the transmission of the effects of substituents from the C(4) and C(5) positions to the C(2) position was noted for the first time and, what is particularly interesting, a difference was observed between the electronic conductivities on the pathway from the C(5) position to the C(2) position and in the opposite direction. Unfortunately, the correlation coefficients and other parameters of the statistical treatment are not quoted in this excellent investigation.

The influence of substituents on the thermal dissociation of the dimers (XV) and (XVI) has been studied in fair detail.[65–73]



(XV)



(XVI)

It has been reported that the constant for the equilibrium between compound (XV) and the corresponding free radical does not obey the Hammett equation,[65] but subsequently these results were disproved.[73] The activation energy for the dissociation of the majority of the dimers investigated is in the range 17–23 kcal mole$^{-1}$.[69] The rate constants for the dissociation of the dimers (XV) and (XVI) are well correlated with the $\sigma$ constants.[66–73] The isokinetic temperature has been calculated on the basis of these correlations.[66] However, it cannot be regarded as reliable, because the measurements were performed over a narrow temperature range. It has also been shown that the nature of the solvent influences the reaction constants.[72,73]

## V. BENZIMIDAZOLES

The question of the influence of the electronic effects of substituents in the 2-position on the basicities of benzimidazoles has been widely disucssed in the literature.[7,23,41,47,74–78] It has been suggested that this interaction has the character of direct polar conjugation.[74] However, more detailed investigations[7,23,41,75] have shown that better relations are obtained when the $\sigma_m$ constants are used. It is noteworthy that, despite the large number of publications devoted to the study of the influence of substituents on acid–base properties, conclusions have been reached in many instances on the basis of clearly inadequate statistical data. The study of Rabiger and Joullii,[76] who investigated the basicities of two series of 5(6)- and 4(7)-halogenobenzimidazoles (four compounds in each series) is instructive in this respect. Both the character of the substituent and the number of compounds preclude any serious generalisations. Nevertheless, on the basis of correlations between the basicity indices of 4(7)-substituted benzimidazoles and the $\sigma_m$ constants, the authors concluded that the tautomeric equilibrium has shifted, the 4-R-tautomer predominating. However, this conflicts with the available experimental data.[79] The basicity constants of 2-arylbenzimidazoles containing substituents in the aryl fragments are correlated more effectively with the Hammett $\sigma$ constants than with the $\sigma^+$ constants.[47]

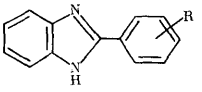
It is of interest that the more pronounced are the electron-accepting properties of the substituent in the 2-position in the benzimidazole ring, the more sensitive is the given series to the electronic effects of the substituents in the phenylene fragment of the molecule.[23] Data based on the two-parameter correlations of the basicity indices and the electronic parameters of the substituents have been published.[42,77,78] The satisfactory ($r$ = 0.993–0.999) correlations between the $pK_{BH^+}$ for the 5(6)-substituted benzimidazole in both one-parameter ($\sigma_m$, $\Sigma\sigma$) and two-parameter ($\sigma_I\sigma_R$, $\sigma_I\sigma_R^0$, $\mathcal{F}\mathcal{R}$) equations[23,77,78] are striking. This is evidence that the thermodynamic stabilities of the 5- and 6-tautomers are similar.

The percentage contribution of the resonance component to the overall transmission of electron effects from the 5(6)-position to the "pyridine" nitrogen atom has been calculated.[78] Regardless of the set of parameters employed ($\sigma_I\sigma_R^0$ or $\mathcal{F}\mathcal{R}$), the percentage of the resonance component is almost the same (37 ± 2% in the former case and 33 ± 2% in the latter). One should therefore consider the numerous instances of the satisfactory correlations between the acid–base properties of the same compounds and $\sigma_m$ constants.[23,41,75]

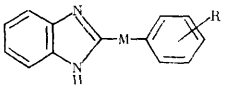
The $\sigma_m$ constant, the nature of which is complex, takes into account the inductive and resonance effects of the substituents with rigorously defined contributions by each. For example, according to Swain and Lupton,[40] the contribution of $\mathcal{R}$ to $\sigma_m$ is 22%. From the foregoing follows the important conclusion that, despite the satisfactory one-parameter correlations with $\sigma_m$ constants,[23,41,75] in the transmission of the effects of substituents in benzimidazoles from the 5(6)-position to the nitrogen atoms in the 1- and 3-positions, the contribution of the resonance component is different from that for the benzene series.[78] Admittedly, the set of substituents employed[38] does not meet the requirements of the "minimum set"[48,53] necessary for a sufficiently reliable separation of the effect into the inductive and resonance components and the above conclusions therefore require further tests on a larger series of compounds.

The acidities of benzimidazole derivative have been investigated.[78,80–87] Data have been published on the acidities of a series of 5(6)-substituted 2-phenyl- and 2-pyridyl-benzimidazoles together with the results of their correlation with the $\sigma_p$ constants.[80–82] The acidities of 4(7)-substituted 2-pyridylbenzimidazoles are correlated with the Taft $\sigma^*$ constants.[82]

The conductivities of certain bridging groups in benzimidazole systems have been studied.[83,84] 2-Arylbenzimidazoles (XVII), whose acidities have been measured potentiometrically, have been used as the standard series. The introduction of the –CH=CH– (XVIII), –S– (XIX), or –$CH_2$– (XX) bridge between the arylene and benzimidazole fragment weakens the electronic influence of the substituent approximately by a factor of two:



(XVII), $\rho_{st}$ = 1.25

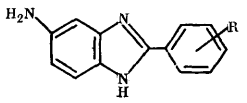


(XVII), $\rho/\rho_{st}$ = 0.60
(XIX), $\rho/\rho_{st}$ = 0.46
(XX), $\rho/\rho_{st}$ = 0.46

The virtually identical conductivities of bridging groups of such different nature are surprising. Compounds of the (XVII)–(XX) series exhibit a spasmolytic activity and for this reason the electronic structures and the hydrophobic properties have been analysed within the framework of the partition coefficient model[88] in order to derive structure–activity relations.[85] It was found that the spasmolytic activity of these compounds is determined predominantly by their hydrophobic properties and is described by a parabolic relation with the hydrophobic constant taken from Leo et al.[88]

1-Methyl-5-R-benzimidazole-2-aldoximes exhibit acidity owing to the presence of the oxime group and their $pK_a$ depend linearly on $\sigma_m$ [86] The results of two-parameter correlations of the $\Delta pK_a$ for the 5-substituted benzimidazoles with the $\sigma_I \sigma_R^0$ constants ($r = 0.989$) and the Swain and Lupton parameters $\mathcal{F}\mathcal{R}$ ($r = 0.992$) have shown, as for the correlation of the $pK_{BH^+}$, that the percentage contribution of the resonance component is virtually identical regardless of the parameters selected.[78] On this basis, one may conclude that the substituent in the 5(6)-position influences both the acid and basic properties via a special mechanism, which differs from that characteristic of the benzene series. Naturally this conclusion requires additional tests on a wider series of compound.

The transmission factor $\gamma$ has been calculated for the series of 2-aryl-substituted 5(6)-aminobenzimidazoles (XXI) from the ionisation constants of the ammonium groups (the reaction state), from the stretching vibration frequencies $\nu$ of the amino-group (the ground state), and from the wavenumbers in the electronic absorption spectra (the excited state).[89]



(XXI)

Analysis of the correlation of the above physicochemical quantities with the Hammett $\sigma$ constants led to the conclusion that the conductivity of the system (XXI) and the excited state is higher than that in the reaction of static states. However, this conclusion is doubtful, since quantities measured in terms of different scales were used in comparing the conductivites. It is noteworthy that, in order to explain the differences between the conductivities of the system (XXI) and the structurally analogous 5(6)-amino-2-(X-phenyl)-benzotriazoles,[89] the authors also used erroneous ideas, assuming that the electronic influences of the substituents in benzimidazoles are transmitted preferentially via the "imine" nitrogen atom.

It has been shown[90] for 2-substituted benzimidazoles that the intramolecular interaction between the substituent and the acidity centre is described quantitatively by the function $pK_a = f(\sigma_m)$ with a correlation coefficient of 0.998.

The differences between the conductivities with respect to the electronic effects of the substituents in the benzene and benzimidazole series were mentioned as early as 1966 in a study,[87] where a correlation was observed between the $pK_a$ for the 5- and 6-substituted benzimidazole and the "mixed" constants $\sigma = \frac{1}{2}(\sigma_m + \sigma_p)$ and $\sigma = \frac{1}{2}(\sigma_m + \sigma_o)$ for the 4- and 7-substituted derivatives.

The electronic influence of substituents and the chemical shifts of the protons of the *N*-methyl group in the $^1H$ NMR spectra of 5-substituted 2-chloro-1-methylbenzimidazoles have been studied.[91] The $^1H$ chemical shifts vary linearly with $\sigma_p$; in the case of solutions in deuteriochloroform the correlations are significantly between when the $\sigma_p^-$ constant is used for the $NO_2$ group, while for solutions in trifluoroacetic acid it is better to employ $\sigma_p$. This difference can be accounted for by the direct polar conjugation of the nitro-group with the indicator centre, while in trifluoroacetic acid the "pyridine" nitrogen atom is protonated.[91] It is of interest that a linear relation between $\delta[^1H(CH_3)]$ and $\sigma_m$ has not been observed for 6-substituted 2-chloro-1-methylbenzimidazoles.[91]

Two-parameter Jaffe and Dewar–Grisdale correlations have led to the hypothesis that the substituents in the 5-position in 1,3-dimethyl-2-benzimidazolones influence the vibration frequency of the carbonyl group and the chemical shifts of the protons in the methyl group mainly via the field effect.[92,93]

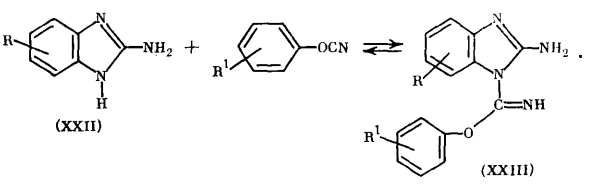
The kinetics of nucleophilic substitution in 2-chlorobenzimidazoles and their salts have been studied.[94–97] 5(6)-Substituted 2-chlorobenzimidazoles react with piperidine, the rate constants for this reaction depending linearly on the "mixed" $\sigma = \frac{1}{2}(\sigma_m + \sigma_p)$ constant.[94] The rate constants for the same reactions of 4(7)-derivatives of 2-chlorobenzimidazoles are correlated with $\frac{1}{2}(\sigma_m + \sigma_o)$.

The study of the kinetics of the substitution of chlorine by piperidine and the methoxide anion in 5- and 6-derivatives of 2-chloro-1-methylbenzimidazole,[95] where the Jaffe equation [Eqn.(4)] was fitted to the reaction rate constants, led the authors to the conclusion that the electronic spectra of the substituents are transmitted from the benzene ring to C(2) position mainly via the "pyridine" nitrogen atom, but the contribution of the "pyrrole" nitrogen atom to the transmission of the electronic influences is also considerable. As will be shown below, the authors lack adequate grounds for this conclusion.

An analogous study has been made for 4- and 7-derivatives of 2-chloro-1-methylbenzimidazole[96] and it was established that, together with the electronic factors, the reaction rate constants are influenced also by the steric effects of the substituents.

The rate constants for the nucleophilic substitution of chlorine in the perchlorates of 5-substituted 2-chloro-1,3-dimethylbenzimidazolium derivatives by thiophenol are correlated with the "mixed" $\sigma = \frac{1}{2}(\sigma_m + \sigma_p)$ constants.[97] The substitution of the chlorine atom in an acid medium in the perchlorates of 5- and 6-derivatives of 2-chloro-1-methylbenzimidazolium derivatives was investigated in the same study in their reactions with thiophenol. Statistical treatment of the results in terms of the Jaffe equation (4) led the authors to the conclusion that the effects of the substituents are transmitted from the benzene ring via the "pyrrole" nitrogen atom to the extent of 39.3%.[97] This conclusion cannot be regarded as sufficiently well-founded (see below). It is of interest to note that the $\sigma_p^-$ constant is used in these correlations for the $NO_2$ group in the 2-chloro-1-methyl-5-nitrobenzimidazolium cation, while in the correlations of the chemical shifts of the protons in the $N-CH_3$ group the $\sigma_p$ constants are employed[91] (see above). The kinetic measurements were performed in aqueous methanol and the $^1H$ NMR spectra were recorded in trifluoroacetic acid and the differences between the solvating capacities of these solvents in relation to the $-\overset{+}{N}H=$ group was in fact the reasons for the necessity to employ different $\sigma$ constants.

In the study of the kinetics of the addition of substituted 2-aminobenzimidazoles (XXII) to aryl isocyanates, it was observed that the rate constants for the consumption of compound (XXII) ($k_2^V$) and the formation of compound (XXIII) ($k_2^E$) vary linearly with the $\sigma$ constants of the substituents R [98] and that the best correlations are obtained when the $\sigma_p$ constants are used for electron-donating substituents and $\sigma_m$ constants for electron-accepting substituents.



(XXII) (XXIII)

The reaction mechanism proposed by the authors, which involves the formation of a six-membered transition state, is confirmed by the negative values of $\rho$ in the regression equations, indicating the acceleration of the reaction by electron-donating substituents:

$$\lg k_2^V = -1.66\sigma + 2.07 \quad (r = 0.995),$$
$$\lg k_2^E = -1.22\sigma + 2.04 \quad (r = 0.999).$$

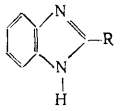
The $^{13}C$ NMR spectra of 5(6)-substituted benzimidazoles have been studied comparatively recently,[99] and it has been shown that the $\delta$[C(2)] are very satisfactorily correlated both with the $\sigma_p$ constants and the "naphthalene" constants $\sigma_6$. In the same study it was noted that the $\delta$[C(8)] vary linearly with the constants $\sigma_p$ and $\sigma_p^+$.

In order to infer the character of the transmission of the electronic influence of substituents in the opposite directions in benzimidazole derivatives, the correlation of the C[5(6)] chemical shifts in 2-substituted benzimidazoles and the C(2) shifts in their 5(6)-isomers was traced:[100–102]

$$\delta[C(5(6))] = (0.80 \pm 0.06)\delta[C(2)] + 8.19,$$
$$r = 0.981,\ S = 0.37,\ n = 7.$$

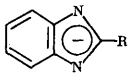
The high correlation coefficient in this equation indicates that the electronic effects of substituents in benzimidazole systems are transmitted in opposite directions via the same mechanism. However, the value of $\rho$ shows that the intensity of the transmission of the effects of substituents from the 2-position to the 5(6)-position is weaker by approximately 20% than in the opposite direction. This non-equivalence is apparently caused by the different environments of the C(2) and C[5(6)] atoms.

The transmission of the electronic influences of substituents in 2-substituted benzimidazoles (XXIV), their anions (XXV),[100,103] 2-substituted 1,3-dimethylbenzimidazolium perchlorates (XXVI),[104] 2-substituted 1-methylbenzimidazoles (XXVII),[105] and 2-substituted 5(6)-nitrogenzimidazoles (XXVIII)[101] has been investigated by $^1H$ and $^{13}C$ NMR:



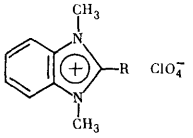
(XXIV)

R = $N(CH_3)_2$, $NH_2$, $OCH_3$, $CH_3$, $C_2H_5$, $SCH_3$, $C_6H_5$, H, Cl, $COOCH_3$, $COCH_3$, $CF_3$, $NO_2$



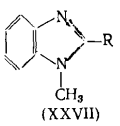
(XXV)

R = H, $CH_2OH$, Cl, $COOCH_3$, $COCH_3$, $C_3F_7$, $CF_3$, $NO_2$



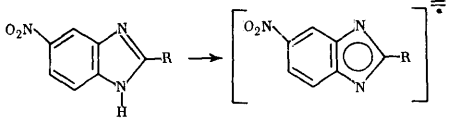
(XXVI)

R = $N(CH_3)_2$, $NH_2$, $CH_3$, $C_2H_5$, $SCH_3$, $C_6H_5$, H, Cl, $COCH_3$, $CF_3$



(XXVII)

R = $NH_2$, $OC_2H_5$, $OCH_3$, $CH_3$, $C_2H_5$, H, Cl, $CF_3$, $COOCH_3$, $COCH_3$, CN, $SO_2CH_3$, $NO_2$



(XXVIII) (XXIX)

R = $N(CH_3)_2$, $NH_2$, $OCH_3$, $OC_2H_5$, $CH_3$, $C_2H_5$, H, Cl, $COCH_3$, $CF_3$, CN

In the above studies the chemical shifts of the protons and $^{13}C$ carbon nuclei of the benzimidazole ring were subjected to a regression analysis using two-parameter correlation equations and various sets of substituent constants ($\sigma_I\sigma_R$, $\sigma_I\sigma_R^0$, $\mathcal{FR}$, etc.) and it has been shown that the electronic influences of substituents are transmitted via the benzimidazole ring of the neutral molecule[100,101,105] and the cation[104] in accordance with the same mechanism. Under these conditions, the resonance mechanism plays a more important role in the transmission of the effects of substituents in the 4- and 7-positions in the benzimidazole ring in all the series investigated than in the 5- and 6-positions. The introduction into the correlation equation of a third semiempirical parameter Q, which takes into account magnetic shielding together with the electronic factors,[106] appreciably improves the correlation coefficients. Nevertheless, it is difficult to infer the contributions of a particular effect owing to the linear relation ($r > 0.9$) between the resonance and Q constants.[100,105] The attempts to replace $\sigma_I$ in correlation equations by the constant $\iota$ [107,108] resulted in the impairment of the correlation coefficients.[100,105]

It is of interest that, in contrast to the neutral molecules (XXIV), in the benzimidazole anions (XXV) the electronic effects of substituents are transmitted exclusively via the resonance mechanism.[100] It may be that this effect is associated with the presence of a delocalised negative charge on the molecule, which can increase the polarisability as a whole.

Attempts have been made with the aid of Eqn.(4) to establish the direction of the transmission of the electronic effects of substituents in certain condensed heterocyclic systems.[24,95–97,109,110] Formal analysis of the results of the two-parameter correlation of the $^{13}C$ NMR shifts of 2-substituted 1-methylbenzimidazoles (XXVII) in terms of Eqn.(4) led to the unexpected conclusion that the electronic effects of the substituents are transmitted from the 2-position to the 5-position mainly via the "pyrrole" nitrogen atom, while the transmission to the 6-position is via the "pyridine" nitrogen atom.[105] However, this conclusion is not reliable, because a linear relation between the parameters $\sigma_m$ and $\sigma_p$ is observed for the series of compounds investigated (with a partial correlation coefficient $r_{12} = 0.959$). According to Jaffe, $r_{12} < 0.9$ serves as a criterion of the applicability of Eqn.(4).[2] By varying the set of points, it is possible to reduce $r_{12}$ only to 0.896,[104] but this leads to a series of substituents which do not satisfy the "minimum set" requirements.[48,53] Thus, it is not possible to reach correct conclusions in terms of Eqn.(4) about the involvement of the "pyridine" and "pyrrole" nitrogen atoms in the transmission of the effects of substituents.

Unfortunately the partial correlation coefficients have not been analysed in the above investigations,[95–97,109] etc., where it was concluded on the basis of Eqn.(4) that the effects of substituents are predominantly transmitted via the "pyridine" nitrogen atom in benzazoles, although such partial coefficients are greater than 0.9, which throws doubt on the validity of the conclusions reached. However, these erroneous ideas have found their way into certain reviews[3] and monographs.[1] Thus the question of the role of a particular heteroatom in the transmission of the electronic influences of substituents remains open.

It is therefore useful to consider a study[111] in which data obtained by studying the transmission pathways of the electronic effects in benzothiazoles with the aid of Eqn.(4) have been analysed. It was shown that the use of this equation can lead to mutually exclusive results: ranging from the insulating influence of the sulphur atom in the transmission of electronic effects to its greater activity compared with the nitrogen atom. However, the relation between the arguments in Eqn.(4) is not analysed in the above study either and yet such analysis would throw light on the causes of the above contradiction. It is noteworthy

that the partial correlation coefficients for all the set of substituents employed by the authors of the communcations quoted by Attanasi et al.[111] are high and likewise preclude a reliable conclusion about the involvement of nitrogen or sulphur atoms in the transmission of the electronic effects of substituents.

In 2-substituted 1-methylbenzimidazoles (XXVII) the substituent is in the *ortho*-position relative to the N–$CH_3$ group. The simple Hammett equation is not applicable to the *ortho*-derivatives,[112] but Charton has shown that two-parameter correlation equations with the constants $\sigma_I$ and $\sigma_R$ in general describe satisfactorily the electronic effects of substituents for *ortho*-derivatives and an additional parameter taking into account the size of the substituent is necessary only in a few instances.[113] The results of the two-parameter correlation of the $\delta(NCH_3)$ in the series (XXVII) with different sets of substituent constants ($\sigma_I\sigma_R$, $\sigma_I\sigma_R^0$, $\iota\sigma_R$, $\mathcal{FR}$) show that the electronic influences of substituens are transmitted to the methyl group via the "pyrrole" nitrogen atom with approximately equal contributions by the inductive and resonance components.[105]

The electronic effects of substituents in the neutral molecules of 2-substituted 5(6)-nitrobenzimidazoles (XXVIII) and in their radical-dianions (XXIX), generated electrochemically, are transmitted to the nitrogen atoms of the nitro-group by the same mechanism according to $^{15}N$ NMR and EPR data with approximately equal contributions by the inductive and resonance components.[101]

In connection with the above data, it is of interest to compare the conductivities of the benzimidazole ring in 5(6)-nitrobenzimidazoles with the conductivities of the benzene ring in *para*- and *meta*-substituted nitrobenzenes. For this purpose, the results of the regression analysis of the $^{15}N$ chemical shifts of the nitro-group in the above compounds were compared.[101,114] Since Craik et al.[114] do not quote the contributions of the inductive and resonance components, an additional statistical treatment of the $\delta(^{15}N)$ for *para*- and *meta*-nitrobenzenes was carried out in terms of the two-parameter equation using the $\sigma_I\sigma_R$ and $\sigma_I\sigma_R^0$ constants. The results proved to be extremely unexpected. Regardless of the set of the inductive and resonance constants the electronic influences of the substituents in both the *para*- and *meta*-positions are transmitted to the nitrogen atom of the nitro-group with approximately the same contribution of the resonance component (approximately 20%). Thus the nitro-group is apparently more strongly conjugated with the benzimidazole fragment in compound (XXVIII) than with the benzene ring in the *para*- and *meta*-derivatives of nitrobenzene.

The electronic influence of substituents on the HFS constants of the protons in the 4-, 6-, and 7-positions in the radical-dianions (XXIX) is not exerted in the same way, their effects on the H(4) and H(7) HFS constants being exerted to a greater extent via the resonance mechanism regardless of the sets of the inductive and resonance parameters of the substituents employed.[101] It has been shown that allowance for the radical-stabilising factor $\sigma^{\cdot}$ [115] improves the correlation coefficients, while the contribution of $\sigma^{\cdot}$ to the transmission of the effects of substituents for H(6) and heterocyclic nitrogen atoms is ~30%.[101]

The $pK_a$ for the 2-substituted 5(6) nitrobenzimidazoles (XXVIII), determined by potentiometric titration, depend mainly on the inductive effects of the substituents.[116] The correlation analysis of the polarographic data for these compounds has shown that the influence of substituents on the $E'_{1/2}$ is exerted via both the inductive and resonance mechanisms with approximately equal contributions by each, while the effect on $E''_{1/2}$ is mainly via the resonance mechanism (85 ± 5%) regardless of the set of parameters of the substituents ($\sigma_I\sigma_R$, $\sigma_I\sigma_R^0$, $\sigma_I\sigma_R^+$, $\mathcal{FR}$). The quantities $E_{1/2}$ are in their turn satisfactorily correlated ($r = 0.987$) with the energies of the LUMO calculated theoretically.[116]

The results of two-parameter correlations of the dipole moments of 2-substitued 5(6)-nitrobenzimidazoles, calculated by the MINDO/3 method using various sets of parameters of the substituents, have shown that the inductive and resonance effects make approximately equal contributions to the overall influence of the substituent.[117,118]

## VI. AZOLES WITH TWO DIFFERENT HETEROATOMS

The acid ionisation of 2-substituted thiazole-4- and thiazole-5-carboxylic acids and the alkaline hydrolysis of their esters have been studied[119] and it has been noted that the $pK_a$ and the rate constants for the hydrolysis of 2-substituted thiazole-4-carboxylic acids are correlated with the $\sigma_m$ constants, while in the case of the 2-substituted thiazole-5-carboxylic acids the correlation is with the $\sigma_p$ constants. The acidities of 2-arylthioazole-4-carboxylic acids in aqueous ethanol solution with different alcohol contents were investigated later.[120] With increase of the content of ethanol in the system, the reaction constant increases somewhat, which can be accounted for by the increased planarity of the arylene and thiazole rings.

It has been noted that the enthalpy of ionisation of alkylthioazoles varies linearly with the constant $\sigma^*$.[121]

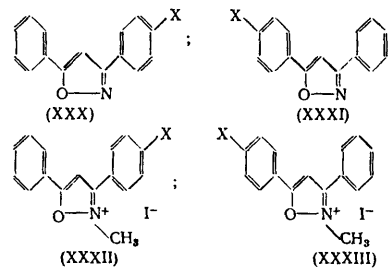
The basicities of 2- and 5-substituted thiazoles have been studied in greater detail by Forlani et al.[122] The authors used the $\sigma_m$ constants for the correlation and concluded that the substituent in the 2-position interacts with the nitrogen atom via the resonance and inductive mechanisms, with the latter predominating. The reaction constants for 2- and 5-substituted thiazoles ($\rho = -9.9$ and $-6.0$ respectively) are comparable to those for other nitrogen-containing heteroarylenes. It is of interest that 2-amino- and 2-dimethylaminothiazoles deviate from the overall correlation, which may be due to the fact that their protonation involves the endocyclic nitrogen atom. The influence of substituents on the acid–base properties of 2-aminothiazoles has also been studied in other investigations.[123,124] Since the reaction constants for two different series—5-substituted 2-amino and 2-dimethylamino-thiazoles—are similar, the authors concluded that the amine–imine tautomerism does not occur in 2-aminothiazoles.[124] The legitimacy of the use of the $\sigma_m$ constants in these series has been confirmed by the results of two-parameter correlations ($\rho_I/\rho_R \cong 0.5$), the endocyclic nitrogen atom proving to be the protonation centre.

The basicity constants of isoxazoles are also correlated with the $\sigma_m$ constants.[125] The dipole moments of 4-substituted 3,5-dimethylidoxazoles are also satisfactorily correlated with the $\sigma_m$ constants.[126]

The influence of substituents on the $^1H$, $^{13}C$, and $^{14}N$ chemical shifts for the substituted oxazoles has been studied[127] and linear relations have been observed between the corresponding $\delta(^{13}C)$ for 4,5-disubstituted oxazoles and the *ortho*-disubstituted benzenes. The possibility of calculating $\delta(^{13}C)$ from the three parameters $\Delta[C(2)]$, $\Delta[C(4)]$, and $\Delta[C(5)]$ characterising the contributions of substituents to the shielding of the C(2), C(4), and C(5) carbon atoms has been demonstrated.

The 3,5-diarylisoxazoles (XXX) and (XXXI) and their quaternary salts (XXXII) and (XXXIII) have been studied by $^1H$ [128–131] and $^{13}C$ [132,133] NMR. Both the one-parameter correlations of $\delta[H(4)]$, $\delta[C(4)]$, and $\delta[C(5)]$ with the $\sigma^+$ constants and the two-parameter correlations using $\sigma_I\sigma_R$ for neutral molecules[132] and $\sigma_I\sigma_R^*$ for quaternary salts[133]

proved to be excellent. It was shown that the sensitivity to the influence of substituents is smaller by a factor of three in the series (XXXIII) than in the series (XXXII) for both $\delta$[H(4)] and $\delta$[C(4)] [128,133] and that the mechanisms of the transmission of the electronic effects in these series is apparently unaltered. However, compared with the neutral molecules of compounds (XXX) and (XXXI), an increased sensitivity of $\delta$[C(4)] to the electronic influence of the substituent has been observed only in the series (XXXII).[133]




In a series of investigations Noyce and co-workers[134–136] studied the solvolysis of ring-substituted 1-thiazolylethyl chlorides.[134–136] The solvolysis rate constants for the substituted 1-(5-thiazolyl)ethyl chlorides are extremely satisfactorily correlated with the $\sigma_p^+$ constants.[134,135] On the basis of two-parameter correlations between the solvolysis rate constants and $\sigma_I\sigma_R$ or , the authors concluded that the resonance effects predominate over the inductive effects in the above reaction of substituted 1-(4-thiazolyl)-ethyl chlorides.[136]

Nucleophilic substitution in 2-chlorothiazoles has been studied.[137–139] The rate constants for the substitution of chlorine in 4- and 5-substituted 2-chlorothiazoles on treatment with thiophenol in acid and alkaline media are correlated with the Hammett $\sigma$ constants,[137,138] the $\sigma_m$ and $\sigma_p$ constants corresponding to the substituent in the 4- and 5-positions respectively. In an acid medium, the rate-determining stage of the reaction is protonation of the thiazole ring.[138] Somewhat later the interaction of 4-substituted 2-chlorothiazoles with the methoxide and thiophenoxide anions was investigated, using $\sigma$ constants, as in previous studies.[139]

The polarographic reduction of 2-amino-4-aryl-5-phenylisothiazoles has been investigated.[140] The substitutents in the phenylene fragment influence the polarographically active azo-group via the thiazole ring, although the absolute value of the reaction constant is low (0.12). In the polarographic reduction of 4-arylisoxazoles, the half-wave potentials are correlated with the $\sigma$ constants of the substituents in the aryl fragment.[141,142]

The study of the influence of substituents on the reaction constants and the physicochemical characteristic of condensed azoles with two different heteroatoms has involved mainly benzothiazole and benzoxazole derivatives. The ionisation constants of 5- and 6-substituted benzothiazolecarboxylic acids[143] and benzoisoxazole-3-carboxylic acid[144] are correlated with the Hammett $\sigma$ constants. The $\sigma_m$ and $\sigma_p$ constants correspond respectively to the substituents in the 5- and 6-positions.[143,144] From this, the authors[143] concluded that the sulphur atom has an insulating effect; the electronic influences of the substituents are transmitted from the benzene ring to the 2-position mainly via the nitrogen atom.

The dissociation constants of 2-benzoxazolines in 2-benzoxazolinethiones have been measured in solution in aqueous acetone.[145] The correlation of the $pK_a$ based on the Hammett and Jaffe equations led to the conclusions that the the compounds exist in the benzoxazoline and the benzoxazolinethione forms and not in the lactim and thiolactim forms respectively.

The basicities of 2-aryl-substituted benzoxazoles and benzothiazoles have been measured in acetonitrile[47] and it has been shown that the basicity constants of the above compounds are correlated best with the $\sigma^+$ constants, while for the corresponding imidazoles and benzimidazoles the best correlation is observed with the $\sigma$ constants.[47] The conductivities with respect to the electronic effects in 2-arylbenzoxazoles and 2-arylbenzothiazoles have been compared with those in 2-arylimidazoles and 2-arylbenzimidazoles on the basis of two-parameter correlation equations. The transmission of the resonance effects of substituents in the aryl fragment to the imidazole and benzimidazole rings is more intense than the transmission of the influences to the oxazole and thiazole rings, which can be accounted for, according to the authors, by the smaller involvement of the oxygen and sulphur atoms in the conduction of the effects of substituents.[47]

The basicities of a series of carbocyanine dyes based on benzothiazoles have been measured and a satisfactory correlation between the basicity constants and the $\sigma_p$ constants has been demonstrated.[146,147] The influence of substituents in the polymethine chain on the absorption spectra of such dyes has been studied with the aid of two-parameter correlations, which led to the observation that the effects of substituents are transmitted mainly via a resonance mechanism.[148,149]

The relation between the $^1H$ or $^{13}C$ chemical shifts and the electronic effects of substituents in various benzoazoles has been studied in a number of investigations.[150–154] The relation between $\delta[^1H(2)]$ and the effects of substituents in benzothiazoles in positions ranging from 4 to 7 was first reported by Taddei et al.[150] Later a linear relation was observed between the chemical shifts of the protons in the methyl group in the 5- and 6-positions in 2-methylbenzothiazoles, 2-methylbenzoxazoles, and 2-methylbenzoselenazoles and the $\sigma$ constants.[151,152] The influence of substituents in benzothiazoles was studied in greater details in two investigations.[153,154] It was shown that the C(4) and C(5) chemical shifts in 2-substituted benzothiazoles are linearly related to the $\sigma_p$ constants ($r$ = 0.9945 and 0.9862 respectively).[153] Three-parameter correlation equations relating $\delta(^{13}C)$ and the parameters $\mathcal{F}$, $\mathcal{R}$, and $\mathcal{Q}$ are quoted in the same communication. Unfortunately these results do not allow the separate estimation of the influences of the inductive and resonance components on the chemical shifts, since $\mathcal{R}$ and $\mathcal{Q}$ are linearly related and the results of two-parameter correlations are not presented. It has been established with the aid of the Jaffe equation (4) [154] that the electronic effects of substituents are transmitted to the benzene and thiazole ring mainly via the nitrogen atom. Shegal et al.[154] arrived at an analogous conclusion. Since the partial correlation coefficients between the arguments are not quoted in the above studies, this conclusion requires additional confirmation. It has also been observed[154] that the intensity of the transmission of the electronic effects of substituents from the 2-position to the 6-position in the benzothiazole ring is weaker by 1/3 than in the opposite direction.

The frequencies of the symmetrical and antisymmetrical stretching vibrations of the amino-group have been measured for twelve 6-substituted 2-aminobenzothiazoles.[156] Having interpreted the results in terms of Eqn.(4) the authors also concluded that the electronic effects of substituents are transmitted to the amino-group preferentially via the nitrogen atom. The transmission factor for benzothiazole, which

is in the range 0.33–0.37, indicating a weaker transmission of the effects of substituents by the benzothiazole ring compared than by the phenylene ring, was determined in the same study.

The investigation of the IR spectra of 2-subsituted benzothiazoles showed that the intensity of the C=N stretching vibrations is linearly related to $(\sigma_R^0)^2$.[157]

A linear relation has been observed between the two-electron reduction potentials of 2-aminobenzothiazoles in the presence of various metal ions and the sum of the Hammett constants.[158] The positive value of $\rho$ indicates a nucleophilic mechanism of the electrochemical reaction. The authors believe that the $\diagdown$C=NH double bond of the imino-tautomer is reduced, although it is known that 2-aminobenzothiazoles exist in the amino-form.[159,160]

Nucleophilic substitution in 4–7-substituted 2-halogenobenzothiazoles has been studied.[109,161–165] The rate constants for the nucleophilic substitution of the halogen by sodium methoxide or piperidine in 5- and 6-substituted 2-halogenobenzothiazoles are correlated with the usual Hammett $\sigma$ constants.[109,161] On the other hand, special $\sigma_4$ constants were introduced for 4-substituted 2-halogenobenzothiazoles and were subsequently employed for the correlation of the rate constants for the oxidation of 4-substituted 2-mercaptomethylbenzothiazoles.[162] The rate constants for the hydrolysis of 2-aryl-6-isothiocyanatobenzothiazoles are linearly related to the $\sigma$ constants of the substituents.[166] The reaction constant for this series ($\rho$ = 0.50) is virtually identical with the reaction constant ($\rho$ = 1.51) determined for the addition of glycine to 2-aryl-6-isothiocyanatobenzothiazoles.[166] The half-wave potentials for the reduction of these compounds also depend on the $\sigma$ constants.[167]

The base-catalysed hydrogen exchange in the 2-position in benzazoles has been studied in a series of investigations.[111,168,169] The rate constants for the proton exchange are satisfactorily correlated with Hammett $\sigma$ constants,[168] while in the case of 6-substituted derivatives it is necessary to employ two-parameter correlations based on the Jaffe equation.[111] The earlier studies,[109,165] in which it was claimed that the electronic effects of substituents in benzothiazoles are transmitted from the phenylene ring to the 2-position exclusively via the "aza" group were examined critically in two investigations.[111,169] Attanasi et al.[111] acknowledged the appreciable role of the sulphur atom in the transmission of the electronic effects of substituents, but their conclusions are based on the results involving the use of the two-parameter Jaffe equation (4) without the analysis of the correlations between the arguments (see above).

## VII. AZOLES WITH THREE AND MORE HETEROATOMS

A detailed analysis of the transmission of the influences of substituents in the series of 1,2,4-triazoles has been carried out in a study[170] where the concept of the limited applicability of one-parameter correlation equations to heterocyclic compounds was developed. Data published previously[171,172] on the quantitative allowance for the influence of substituents in the triazole ring on the physicochemical properties and reaction rates were treated in terms of the two-parameters equation using the $\sigma_I$ and $\sigma_R$ constants. The results show that the inductive effects predominate over the resonance effects.[170] However, it is extremely difficult to make correct estimates owing to the lack of knowledge about the absolute errors in the coefficients of the arguments.

The acidities of C-substituted 1,2,4-triazoles have been studied in relation to five different series[170,172–174] in which the influence of substituents on the acidity constants was taken into account mainly in terms of the inductive mechanism. However, the resonance influence of the substituent cannot be neglected either except in those cases where the system ceases to be aromatic.[170,174]

The data on the correlations of the acid–base properties of substituted tetrazoles and the electronic parameters of the the substituents published after 1978 have been described in a series of studies[43,175–183] and have been surveyed in a review.[184] On the basis of the effective correlations of the $pK_a$ for several series of 5-substituted tetrazoles and various $\sigma$ constants, the authors[177,178] concluded that the compounds indicated exist in a single tautomeric form (1-H). The correlations of the $pK_{BH^+}$ and the $\sigma$ constants for a different series of tetrazole derivatives, taking into account the correlation of the charge density on the nitrogen atoms and the $\sigma_p$ constants,[180] established that the tetrazole ring is protonated at the nitrogen atom in the 4-position.[176,181–183] These investigations were continuned in subsequent years in relation to aryltetrazoles and tetrazolylacetic acid.[185–187] Excellent correlations have been found between their $\Delta pK_a$ and the Swain and Lupton parameters for both *meta*- and *para*-derivatives.[185] The $pK_{BH^+}$–$\sigma$ correlations observed[186] confirmed the earlier hypothesis concerning the protonation centre of the tetrazole ring.

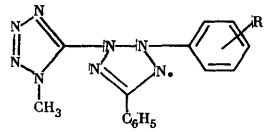
It has been shown for 5-R-tetrazoles that the influence of substituents on the acidity and basicity of these compounds is manifested in the same way; a satisfactory linear relation has been observed between their $pK_a$ and $pK_{BH^+}$,[188] which permits a quantitative estimation of the acid–base properties of 5-substituted tetrazoles.

The influence of substituents on the position of the long-wavelength maximum in the electronic spectra of 1-methyl-3-nitro- and 1-methyl-5-nitro-1,2,4-triazoles.[170,189] The electronic and infrared spectra of 5-aryltetrazoles have been investigated by a group of Polish workers,[190,191] who correlated different frequencies in the spectra of these compounds with the $\sigma$ constants, but the correlation coefficients obtained are as a rule low.

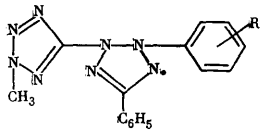
The chemical shifts of the protons in the $^1H$ NMR spectra of 3(5)-substituted 1,2,4-triazoles are linearly related to the $\sigma_p$ constants.[192] It was demonstrated later that the correlations of the inductive and resonance components to the overall transmission of the effects of substituents are approximately the same.[170] Attempts have been made to estimate the influence of substituents on the chemical shifts of the protons in the methyl group in 3-substituted 1-methyl-5-nitrotriazoles,[173,193] but the correct analysis of these relations was complicated by the powerful shielding effects. The influence of substituents in the benzene ring on the H(5) chemical shifts in 4(5)-aryl-1,2,3-triazoles and 1-amino-4-aryl-1,2,3-triazoles has been studied.[194] It is noteworthy that the reaction constants for the above series of compounds are virtually identical (0.35 and 0.36 respectively). What is in essence the converse problem has been solved in a study[195] where the influence of the tetrazolyl group on the chemical shifts of the protons in the phenylene ring was investigated and the Swain and Lupton constants were calculated for the 5-tetrazolyl fragment.

A linear dependence of the spin–spin coupling constants $j'$[C(5)H] and the $\delta$[C(5)] chemical shift for the 1-substituted tetrazoles on the $\sigma_I$ constants has been observed by $^1H$ and $^{13}C$ NMR.[196]

The satisfactory correlations between the nitrogen HFS constants in the EPR spectra of the radicals (XXXIV) and (XXXV) indicate that the variation of the parameters of the isotropic HFS by the N(3) atom is determined by the electronic influence of the substituents, while the geometry of the radicals does not change significantly.[197]



(XXXIV)



(XXXV)

The influence of the solvent on the transmission of the electronic effects of substituents in *para*-substituted 4-aryl-1,2,4-selenodiazoles has been investigated with the aid of the Swain and Lupton parameters.[198] It was then shown by $^1$H NMR that the nature of the solvent does not have a significant influence on the ratio of the contributions of the inductive and resonance components in the overall transmission of the substituent effects.

The ionisation potentials of 3,5-diphenyl-1,2,4-oxadiazoles substituted in the 3- or 5-phenyl rings are linearly related to the $\sigma^+$ constants.[199] In later studies, the authors showed that only the intensity of the peaks due to the aroyl ions in the mass spectra of 5-amino-3-aroyl-1,2,4-oxadiazoles is correlated with the $\sigma^+$ constants albeit with a low correlation coefficients.[200]

In relation to the nucleophilic substitution of the nitro-group in 3-substituted 1-methyl-5-nitro-1,2,4-oxadiazoles 5-substituted 1-methyl-3-nitro-1,2-triazoles, it has been observed that the intensity of the transmission of conjugation effects from the 5- to the 3-position is approximately three times greater than in the opposite direction, while the inductive influence of substituents is transmitted to virtually identical extents in both directions.[170,201]

Alkylation of substituted 5-aryltetrazoles and their potassium salts by dimethyl sulphate[202,203] or ethyl bromoacetate[204] showed that the ratio of the 1- and 2-isomers in the reaction product is correlated with the $\sigma$ constants of the substituents in the benzene ring. Electron-accepting substituents inhibit the reaction and increase the fraction of the 2-isomer. An analogous behaviour has been observed in the alkylation of 5-aryltetrazoles by methyl iodide under the conditions of phase-transfer catalysis.[205] However, similar correlations have not been observed in the alkylation by dimethyl sulphate in a two-phase system. These data led to the conclusion that the alkylation of tetrazoles by methyl iodide takes place in the organic phase, while the alkylation by dimethyl sulphate takes place in both the organic and aqueous phases.

The rate constants for the substitution of the hydrogen in the methyl group by deuterium in 5-methyl-1-(R-phenol)-tetrazoles are correlated with the substituent constants $\sigma^0$ ($\rho = 3.0$).[206,207]

The half-wave potentials for the reduction of 1-amino-4-(X-aryl)-1,2,3-triazoles, 1-H-4-(X-aryl)-1,2,3-triazoles,[208] and 1-(X-aryl)-5-mercaptotetrazoles[209] are correlated with the $\sigma$ constants.

Much less information is available about the transmision of the effects of substituents in condensed azoles with three heteroatoms. It has been shown that the $pK_a$ for benzotriazoles are correlated with the Hammett $\sigma$ constants.[23] The half-wave potentials for the reduction of 1-aryl-2-aryl-5-isothiocyanatobenzotriazoles are also linearly related to the $\sigma$ constants, the 2-substituted isomers being reduced more readily and their reaction constants being lower.[167]

Benzothio- and benzoseleno-diazoles have been investigated thoroughly.[210] An approximate correlation has been obtained for these compounds between the positions of the maxima in the electronic absorption spectra and the $\sigma$ constants. Their electrochemical reduction potentials are also correlated with these constants. The replacement of selenium by sulphur increases somewhat the influence of the substituent and the authors believe that the inductive effect plays a decisive role. The intensity of the influence of the substituent is almost independent of its position in the molecule.[210]

The rate constants for the thermal decomposition of benzo-1,2,3-thiadiazole-1,1-diozide, containing substituents in the aromatic ring, are linearly related to the $\sigma$ constants.[211] The attempt by the above authors to estimate the direction of transmission of the effects of substituents with the aid of the Jaffe equation cannot be regarded as successful, in our view, because the relation between the arguments was not analysed.

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The studies quoted in this review are not equivalent as regards their importance. Some of them have been carried out for a series of compounds with a limited set of substituents which we believe reduces the reliability of the results and sometimes leads to clearly erroneous conclusions, as happened, for example, in the study of Rabiger and Joullie.[76] On the other hand, an inadequate statistical treatment can also result in unjustified conclusions.[95,97,111,157,165,212]

In many cases it has been possible to apply the Hammett equation in its original form to various heterocycles. However, arbitrarily selected constants ($\sigma_m$, $\sigma_p$, $\sigma^0$, $\sigma^+$, $\sigma^-$, etc.) were then used without any justification. In other investigations, several different types of constants were compared and the authors inferred their applicability to a specific type of heterocycles on the basis of the correlation coefficient. However, in all cases it is implied that the relative contributions of the inductive and resonance mechanisms to the overall effect of the substituent on the reaction or indicator centre is the same as in benzene derivatives. Where it was not possible to select the type of constants for the benzene series for a quantitative description of the process, special sets of $\sigma$ constants characteristic of the given type of heterocycles only were introduced.[50,162,213] This procedure, involving the specification of a new set of $\sigma$ parameters for each type of heterocycle and for each relative disposition of the substituents and the reaction centre, rules out the possibility of comparing the reactivies of different classes of compounds, is extremely laborious, and vitiates the practical significance of such correlations.

The approach which takes into account separately the influence of the inductive and resonance effects of substituents on the reaction centre with the aid of many-parameter equations is more promising. It has made it possible to discover the specific features of the transmission of the electronic influences of substituents via the benzothiazole,[154] 1,2,4-triazole,[170] and benzimidazole [100-104,214,215] rings.

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# The Present State of the Problem of Silicenium Ions

V.D.Nefedov, T.A.Kochina, and E.N.Sinotova

The present state of the problem of the existence and chemical behaviour of silicenium ions in the gas and condensed phases is examined and the principles of a new (nuclear-chemical) method for the generation of free silicenium ions, its characteristic features, and its advantages are described.
The bibliography includes 144 references.

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## I. INTRODUCTION

The question of the possibility of the existence and the properties, reactivity, and role in the corresponding chemical processes of the silicon, germanium, and other analogues of carbenium ions is one of the most interesting in modern chemistry. The problem of the preparation and investigation of the properties of the silicon analogues of such ions is the most urgent at the present time.

Since silicon is less electronegative than carbon (their electronegativities are 1.8 and 2.6 respectively[1]), it was to be expected that silicenium ions would be formed at least as readily as carbenium ions and this is indeed the case in the gas phase.[1,2] The results of mass-spectrometric studies indicate the preferred formation, on energy grounds, of silicenium ions compared with carbenium ions.[2-4] However, many attempts to obtain silicenium ions in solution failed.[5-7]

Before proceeding to the consideration of various aspects of the problem of silicenium ions, it is essential to note that, apart from the great similarity in the chemical behaviour of silicon and carbon compounds, there exist also differences which can be accounted for in the first place by the presence of unoccupied $d$ orbitals in silicon. The results of numerous investigations have shown that in its chemical behaviour silicon tends to expand its coordination (there is a transition from the $sp^3$ state to the $sp^3d$ or $sp^3d^2$ state) and not to contract it, as happens in the case of carbon (transitions from the $sp^3$ state to the $sp^2$ and $sp$ states).

It was believed for a long time that, in contrast to carbon, silicon is incapable of forming multiple $p_\pi-p_\pi$ bonds. However, since 1967 communications began to be published[8-10] in which the formation of unstable silicon compounds with Si=Si bonds was reported. In 1981-82 the first stable compounds with Si=C and Si=Si bonds were obtained.[11-13] In addition the $p_\pi-d_\pi$ bond, which is unknown for carbon, exists in silicon compounds.[14,15] It arises as a result of a shift of the $\pi$ electrons in a neighbouring X atom (where X is a halogen, an aryl group, oxygen, nitrogen, etc.) to the unoccupied $d$ orbitals of silicon. As a result of such $p_\pi-d_\pi$ bonding, the Si-X bond has a partial double bond character. The smaller length of the Si-X bond compared with the value calculated from the covalent radii, the widening of the valence angle in excess of the usual tetrahedral value, the reduction of the electron-donating capacity of the X atom on formation of a hydrogen bond, etc. are usually regarded as evidence for the $p_\pi-d_\pi$ interaction.[15]

Two aspects must be distinguished in the study of the problem of silicenium ions. The first concerns the possibility of the existence of silicenium ions in crystals and solutions as independent species. The second aspect involves the possibility of the appearance and existence of these ions as intermediate species. The problem of silicenium ions will in fact be considered below in terms of these two main features.

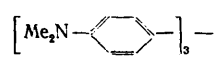
## II. SILICENIUM IONS IN CONDENSED PHASES

### 1. Silicenium Ions as Independent Species in Solutions and Crystals

When attempts were made to demonstrate the existence of silicenium ions, organosilicon compounds which should have given rise to the corresponding ions under suitable conditions, by analogy with carbon compounds, were considered in the first place. Many investigators tried to show that the silicenium ion $Ph_3Si^+$, analogous to the stable ion $Ph_3C^+$, can exist. However, it has been demonstrated by a conductimetric method that there is no appreciable ionisation of $Ph_3SiCl$ in pyridine, in a mixture of nitrobenzene with $AlBr_3$, or in liquid sulphur dioxide, although it is well known that all these solvents induce the ionisation of $Ph_3CCl$:[16]

$$Ph_3CCl \rightarrow Ph_3C^+ + Cl^-.$$

Another attempt consisted in the study of the properties of the silicon analogue of chlorotris(*p*-dimethylaminophenyl)-methane, which is an ionic compound. It was established by means of a number of methods (conductimetry, IR and UV spectroscopy, and X-ray diffraction) that

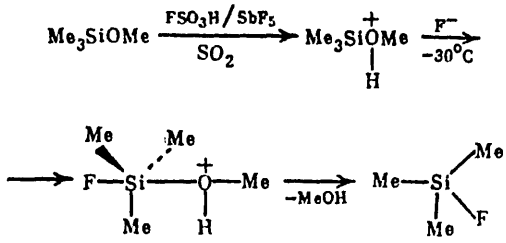


is a covalent compound.[17,18]

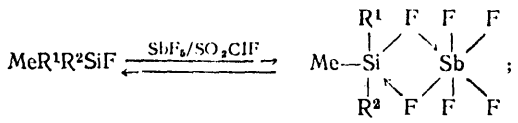
A number of studies were designed to compare and investigate the properties of silicon perchlorates.[19,20] It was demonstrated that the silicon perchlorates $R_3SiClO_4$ (where R = Me, Et, n-Pr, *p*-$MeC_6H_4$, or Ph) have a covalent structure, in contrast to the intensely coloured triarylmethyl perchlorates.

An attempt has been made[21,22] to obtain classical silicenium ions in the $FSO_3H/SbF_5/SO_2$ superacids whose nucleophilic properties are extremely weak. In this medium secondary and tertiary carbenium ions are stable and can be generated from organic compounds of different classes. The behaviour of alkoxysilanes and siloxanes in the above medium was studied at a low temperature by NMR and it was shown that

the oxygen atom is protonated, this being followed by a substitution reaction which leads to fluorosilane. $R_3Si^+$ ions were not detected. The formation of fluorosilanes can be accounted for by the appearance of a pentacovalent intermediate:

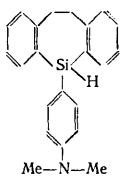


The behaviour of the fluorosilanes $Me_3SiF$ in the $SbF_5/SO_2$. .ClF medium, in which stable carbenium ions can be detected, has also been studied.[23] However, in this case too the silicenium ions $R_3Si^+$ were not detected as independent species. The authors suggested that an involved complex having the following structure may be formed:[23]



$R^1 = R^2 = Me$; $R^1 = Me$, $R^2 = F$; $R^1 = R^2 = F$.

Corey and co-workers[24,25] reported the synthesis of silicenium ions from a compound which they synthesised, i.e.



by abstracting a hydride ion from the latter. However, later these results were disproved.[26,27]

The cause of the failure of the above investigations has apparently been the fact that the authors began with the hypothesis that there is a complete analogy between the properties of carbon and silicon, which is not always justified. For example, it is known that carbenium ions are readily stabilised as a result of the resonance $2p-2p$ transition between the carbenium atom and the ligand atoms linked to it. However, a simple interaction is much weaker in silicenium ions, where the silicon atom is linked to the elements of the Second Period (a resonance $2p-3p$ transition).[28] Calculations have shown that a more effective stabilisation can be achieved as a result of the resonance $3p-3p$ interaction in structures of the type $(RX)_3Si^+$ or $(R_2X)_3Si^+$, where X = S, P, or elements of the Third Period.[29,30] These ideas have been confirmed experimentally by Lambert and Schultz,[31] who attempted to obtain substituted silicenium ions by abstracting a hydride ion from tris(2-propylthio)silane in accordance with the mechanism

$$(iso\text{-}PrS)_3SiH + Ph_3C^+ClO_4^- \rightarrow Ph_3CH + (iso\text{-}PrS)_3Si^+ClO_4^-.$$

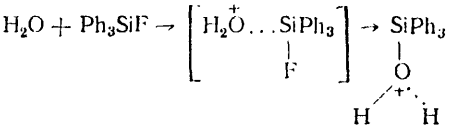
These investigations (conductrimetry, IR and UV spectroscopy, and NMR) led to results which agreed with the hypothesis of the formation of silicenium ions in this reaction.

The set of studies examined, including the last, indicate the lack of a final solution of the problem concerning the possibility of the existence of silicenium ions as independent species and the necessity for its further investigation.

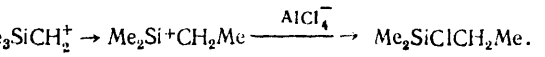
## 2. Silicenium Ions as Intermediate Species in Reactions of Organosilicon Compounds

Apart from the existence of silicenium ions as independent species, their involvement as intermediates in reactions has been frequently postulated. One of the first experiments designed to demonstrate the possibility of the formation of silicenium ions as reaction intermediates has been a kinetic study of the solvolysis of fluorotriphenylsilane.[32] The authors of this investigation observed a marked dependence of the rate of reaction on the nucleophilic properties of the medium. Thus $Ph_3SiF$ reacts ten times faster in the presence of $OH^-$ ions than in a neutral medium (acetone–water), while the rate of hydrolysis of $Ph_3CF$, which is the carbon analogue of the above compound, is independent of the pH of the medium. In addition, *p*-methyl substituents, introduced into fluorotriphenylsilane, decreased the rate of reaction by a factor of five, while their introduction into fluorotriphenylmethane increased the rate of reaction. This shows that a positive charge does not arise on the silicon atom in the transition state.

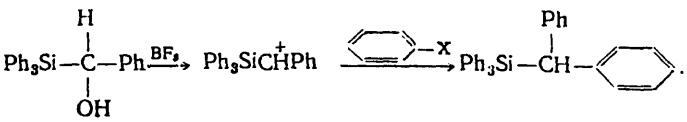
Bearing in mind the foregoing, Swain et al.[32] put forward a mechanism involving the formation of an intermediate pentacovalent silicon complex:



The rearrangement of organosilicon compounds with functional α-groups under the influence of Lewis acids is of interest from the standpoint of the possibility of the formation of silicenium ions as intermediates.[33–35] One of the proposed mechanisms is the Wagner–Meerwein mechanism:

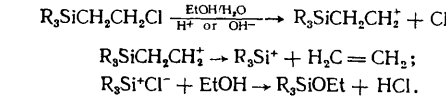


The formation of stable silicon-containing carbenium ions has indeed been demonstrated for these reactions both by direct observation and with the aid of the Friedel–Crafts reaction:[34]

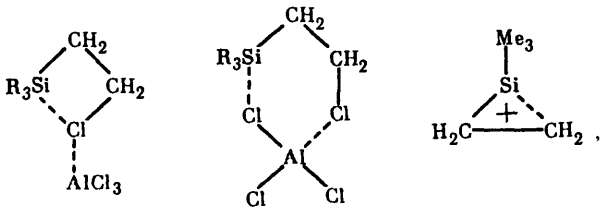


On the other hand, silicenium ions were never detected in these systems.

The hydrolysis of β-halogenoalkylsilanes has been investigated[36] and an ionic mechanism has been proposed for the reaction:



However, in this case too the formation of silicenium ions was not confirmed. The ionic mechanism has been criticised.[37,38] Other explanations of the formation of the observed products were based on the hypothesis that the reaction proceeds via a mechanism involving the appearance of complexes incorporating four-membered (A) or six-membered (B) rings[33] or via a stage in which a non-classical carbenium ion (C) is formed:[38]



(A) (B) (C)

The formation of the latter has been confirmed by the fact that the reactivity of compounds with functional β-groups is much higher than might have been expected as a consequence of the inductive effect of the $Me_3SiCH_2$ group.[39] This means that the C–X bond is cleaved under the influence of precisely the $R_3Si$ group, in agreement with the structure of the non-classical carbenium ion.[38] Despite this, one cannot rule out the possibility that the above rearrangement proceeds via a mechanism involving the formation of silicenium ions, because such ions have been detected in a similar rearrangement in the gas phase.[40]

An ionic mechanism has also been proposed for the disproportionation of halogenosilanes under the influence of Lewis acids:[41–43]

$$R_2SiHCl + AlCl_3 \rightarrow [R_2SiH]^+ + [AlCl_4]^-;$$
$$R_2SiHCl + [R_2SiH]^+[AlCl_4]^- \rightarrow R_2SiH_2 + [R_2SiCl]^+[AlCl_4]^-;$$
$$[R_2SiCl]^+ + [AlCl_4]^- \rightarrow R_2SiCl_2 + AlCl_3.$$

However, no evidence in support of the proposed mechanism was obtained in this case either.

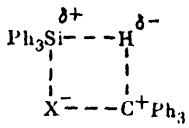
Reactions accompanied by racemisation are of special interest in the study of the possibility of the appearance of silicenium ions as intermediates. In the case of carbon compounds racemisation as a rule indicates the formation of a carbenium ion with the $sp^2$ structure as an intermediate form. However, the reactions are highly stereospecific for silicon compounds (>95%). Even in the presence of substituents such as aryl, vinyl, and allyl[44] a high stereospecificity was observed, indicating the absence of silicenium ions with the classical structure in the reactions of organosilicon compounds. In contrast to this, the analogous carbon compounds racemise very rapidly under solvolysis conditions as a result of the formation of the corresponding carbenium ions. However, one should note that in many cases optically active halogenosilanes do racemise.[45–54]

We shall consider the racemisation of halogenosilanes induced by certain solvents.[48,49] Conductrimetric measurements indicate the absence of any appreciable ionisation. The hypothesis of the formation of an ion pair has been put forward as an explanation, but it proved inconsistent with the absence of conductivity in the reaction medium. Further investigations showed that, among solvents capable of inducing the racemisation of chlorosilanes, there are some with a low dielectric constant, for example ethers ($\varepsilon < 15$), and also polar aprotic solvents.[54] The latter are especially interesting because they behave as effective ligands for elements with unoccupied *d* orbitals, since they form coordinate bonds readily. Analogous results have been obtained for optically active germanium compounds.[55,56] It has been suggested that the racemisation proceeds via a mechanism involving the formation of penta- and hexacoordinate intermediate silicon compounds. This hypothesis has been confirmed by the finding that bulky substituents at the silicon atoms retard the racemisation. The rate of racemisation involving the formation of the $R_3Si^+$ cation should have increased with increasing bulk of the substituents. This has been explained by the fact that, with increase of the bulk of substituents, their mutual repulsion should also increase, which facilitates the formation of the $R_3Si^+$ cation and hinders the formation of penta- and hexacoordinate intermediate compounds.

In order to demonstrate the possibility of the formation of silicenium ions as intermediate species, the hydride transfer reaction has also been investigated.[57–59] The ability of carbenium ions to act as acceptors of hydride ions was used for this purpose.[60] Formally, when a hydride ion is abstracted from silane by a carbenium ion, a silicenium ion, which is an analogue of the carbenium ion, should be formally produced:

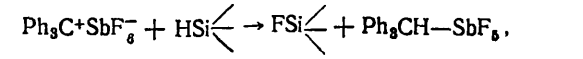
$$Ph_3C^+ + HSiR_3 \rightarrow Ph_3CH + R_3Si^+.$$

However, the appearance of silicenium ions has not been demonstrated for numerous silanes.[57–59,60] On this basis, a mechanism postulating the formation of a complex with a four-membered ring has been proposed for the hydride transfer reactions:[61]



Reactions of this type include the hydrogenation of olefins or the hydrogenolysis of alcohols by silanes in an acid medium.[62,63] Like those examined above, these reactions proceed via the formation of carbenium ions, which then abstract a hydride ion from the silane. However, the formation of silicenium ions in these reactions was also not demonstrated. The absence of silicenium ions as kinetically independent species can apparently be accounted for by the presence in the silicon atom of occupied *d* orbitals, which are responsible for the tendency of organosilicon compounds, including silanes,[64] to associate with nucleophiles with expansion of the outer electron shell.[1]

However, in a study of the kinetics of the hydride transfer from a silane to a carbenium ion in the reaction



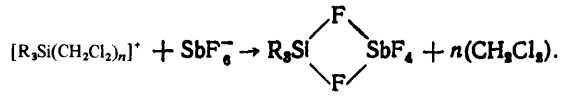
it has been observed[65] that the rate of appearance of the silane $R_3SiH$ is higher than the rate of formation of the fluorosilane $R_3SiF$, which conflicts with the four-centre synchronous mechanism. In addition, it had been shown earlier that the stereochemical course of the reaction depends on the solvent.[58] This shows that the four-centre mechanism may not be the only one possible and does not rule out the possibility of the formation of an intermediate in which the positive charge is localised on the silicon atom.[66] It has been suggested[65] that the reaction proceeds with participation of silicenium ions and involves at least three stages.

The first stage is the hydride transfer leading to the formation of a positively charged silicon intermediate:

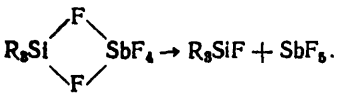
$$Ph_3C^+ + HSiR_3 \xrightarrow{n(CH_2Cl_2)} Ph_3CH + [R_3Si(CH_2Cl_2)_n]^+.$$

The second stage involves the formation of an uncharged

intermediate:

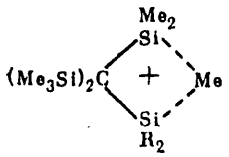


The third stage involves the decomposition of the uncharged intermediate with formation of the final products:



The reactions of organosilicon compounds containing the bulky tris(trimethylsilyl)methyl groups $(Me_3Si)_3C$ have been investigated.[67-70] The presence of these groups gives rise to steric hindrance in the nucleophilic attack on the silicon atom and hence makes it possible to observe reactions of an unusual type.

Thus, when the organosilicon iodides $(Me_3Si)_3CSiR_2I$ react with silver and mercury salts and also with halogens in methanol, the bridged silicenium cation (I)



(I)

is formed according to the authors.[67-70] The cation can also be attacked by nucleophiles, which is accompanied by the formation of rearrangement products of the type $(Me_3Si)_2C(SiR_2Me)(SiMe_2X)$.

A kinetic study of the solvolysis of the silicon perchlorate $(Me_3Si)_3CSiMe_2OClO_3$ has been carried out[71] in the presence of the salts NaOMe, LiCl, $LiNO_3$, and $NaClO_4$. The results of the kinetic investigations of the solvolysis were consistent with an $S_N1$ mechanism. It was suggested that the reaction also proceeds via the formation of the bridged silicenium cation (I).

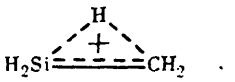
Thus the results of studies of the behaviour of organosilicon compounds in condensed phases are contradictory and, in contrast to carbon compounds, they can be partly interpreted without resorting to the idea that classical silicenium ions are formed as stable species or as reaction intermediates. This is apparently associated with the characteristics of the electronic structure of silicon distinguishing it from carbon (the presence of unoccupied *d* orbitals, the greater size of the silicon atom, its lower electronegativity, etc.) and its high nucleophilicity caused by these features.

## III. SILICENIUM IONS IN THE GAS PHASE

### 1. Energy Relations in the Formation of Silicenium Ions

Whereas all attempts to demonstrate the existence of silicenium ions in the condensed phase have been unsuccessful, the formation of these species is a common phenomenon in rarefied gases, where they arise from organosilicon compounds under the influence of electron impact. Furthermore, the results of studies of the energetic conditions in the formation of tervalent silicenium ions have shown that their stability in the gas phase is greater than that of the analogous carbenium ions. Thus the heat of formation of the $H_3Si^+$ ion is 890 kJ $mol^{-1}$, while the heat of formation of the methyl cation $H_3C^+$ is 1090 kJ $mol^{-1}$.[72] The heat of formation of the $H_3Si^+$ ion has also been published[4] as 970 kJ $mol^{-1}$, which is somewhat greater than the value quoted in the above study[72] but is lower than the heat of formation of the methyl cation. The situation is analogous also as regards substituted silicenium ions. Thus the heat of formation of the trimethylsilicenium ion is 580 kJ $mol^{-1}$,[1] 590 kJ $mol^{-1}$,[3] or 610 kJ $mol^{-1}$ [4] according to the data of different investigators; evidently all these data are in good agreement. On the other hand, the lowest of the known heats of formation of the trimethylcarbenium ion is 680 kJ $mol^{-1}$,[73] i.e. is much higher than that of the trimethylsilicenium ion.

It has been shown[74] that the principal ion formed when methylsilane is bombarded by electrons having an energy of ~100 eV is the methylsilyl cation $MeSiH_2^+$. In the mass spectrum of deuteriated methylsilane $MeSiD_3$, the peak at *m/e* 47, corresponding to the $MeSiD_2^+$ ion, is 10 times higher than the peak at *m/e* 48, corresponding to the $D_3SiCH_2^+$ ion. In addition, non-empirical calculations have shown[75] that the heat of formation of the methylsilyl cation $MeSiH_2^+$ is higher by 190 kJ $mol^{-1}$ than that of the silylmethyl cation $H_3SiCH_2^+$ and by 170 kJ $mol^{-1}$ than that of the non-classical bridged ion



Thus the available theoretical and experimental data agree with one another.

The heats of formation of certain other tervalent silicenium ions have also been determined.[76,77] Thermodynamic calculations using the bond dissociation energies[76] as well as data for the vertical ionisation potentials of the radicals $RSiH_2^{\bullet}$ [76] and $RCH_2^{\bullet}$ [78] have shown that the silylcarbenium ions $H_3SiCH_2CH_2^+$ isomerise exothermically to the ethylsilicenium ions $EtSiH_2^+$ ($\Delta H = -120$ kJ $mol^{-1}$).[77]

Naturally the available information about the heats of formation of various silicenium ions is as yet insufficient, but analysis of the existing data already indicates that the energetic conditions in the formation of silicenium ions in the gas phase are more favourable than in the formation of the analogous carbenium ions.

### 2. Ion–Molecule Reactions of Silicenium Ions

In the general case ion–molecule reactions are understood as interactions of ions with neutral molecules accompanied by a change in either the elemental composition or in the charge or energy state of the species involved in such a process. Depending on the ratio of the time of the interaction (collision) between the ion and the molecule and the characteristic time of the transitions between the states of the colliding species, the mechanisms of ion–molecule reactions are divided into two types: direct reactions[79-86] and reactions proceeding via a mechanism involving the formation of a long-lived complex.[87,88]

Ion–molecule reactions proceed via the direct mechanism when the kinetic energy of the relative movement of the partners exceeds the energy of their polarisation attraction: $E_k > \alpha e^2/2r^4$ (here $\alpha e^2/2r^4$ is the energy of the polarisation interaction of the ion and the molecule over a distance *r*, equal to the sum of the radii of the ion and the molecule, and $E_k$ is the kinetic energy of the relative movement of the ion and the molecule). The simplest model describing the direct mechanism is that of the direct stripping mechanism proposed by Henglein.[86] According to this model, the

transfer of energy from the species to the reactant ion takes place over a very short period. The possibility of the transfer of momentum to the residual species is then ruled out and its velocities before and after collision differ little. In such reactions, it is possible to predict the energy distribution of the products. Thus, when a hydride ion is transferred from the silane molecule to the reactant ion, the kinetic energy of the movement of the product ion is equal to the thermal energy (like the energy of the silane molecules) and the neutral product formed is characterised by the same kinetic energy as the reactant ion (i.e. a considerable energy).

The second type of ion–molecule reactions includes those involving the formation of a long-lived complex.[87,88] The reactions proceed via this mechanism when the energy of the polarisation interaction exceeds the kinetic energy of the relative movements of the ion and the molecule, i.e. subject to the condition $E_K < \alpha e^2/2r^4$; this condition is a criterion of the stability of the complex. The capture of the ion by the polarisation orbital of the molecule, which leads to the mutual approach of the colliding species to distances of the order of atomic dimensions, proceeds via this mechanism for certain parameters of the ion–molecule collision process. For such distances, the kinetic energy of the colliding species can be consumed in the excitation of internal degrees of freedom, which entails the formation of a long-lived complex whose decomposition yields the final products.[87,88]

Numerous mass-spectrometric studies of ion–molecule reactions of silicenium ions have been published recently. These include the investigations of ion–molecules reactions in pure silane,[89–91] in methylsilane,[92,93] in mixtures of silane with organic compounds,[77,94–100] the studies of ion–molecule reactions of carbenium ions with alkylsilanes,[101–103] the study of the intramolecular and intermolecular rearrangements of organosilicon compounds,[40,104–110] and also the study of the ion–molecule reactions of trimethylsilicenium ions with organic and organosilicon compounds.[111–114]

*(a) Ion–molecule reactions in silane and its substituted derivatives.* Studies of the reactions in methane, whose main products are the ions $CH_5^+$ [115] and $C_2H_5^+$,[116] are known to have played a major role in the development of our knowledge about ion–molecule reactions:

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + Me; \quad (1)$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2. \quad (2)$$

In the study of reactions occurring in silane, it is therefore of interest to compare the latter with processes characteristic of methane. Table 1 presents certain data for methane and silane which are of interest for the investigation of the gas-phase ion–molecule reactions of these compounds.

It is seen from Table 1 that, in contrast to methane, silane is not stable in relation to decomposition into its constituent elements. The ionisation of silane requires less energy than the ionisation of methane and much less energy must be expended on the formation of the $SiH_2^+$ and $SiH_3^+$ ions from silane than on the formation of the $CH_2^+$ and $CH_3^+$ ions from methane. The dipole moment of the Si–H bond has the opposite direction and should be much greater than the dipole moment of the C–H bond.

It has been shown[122] that the peak corresponding to the $H_5Si^+$ ion, which is analogous to the $H_5C^+$ ion in the case of methane, is absent from the mass spectra of monosilane (at pressures from $10^{-5}$ to $10^{-1}$ mmHg). Consequently a reaction analogous to reaction (1), in which the $H_5Si^+$ ion might have been formed, does not occur in the case of silane.[122] On the other hand, the absence of the $SiH_4^+$ ion can be readily accounted for with the aid of the data in Table 1. Using the ionisation potentials of the molecules and the appearance potentials of the ions (Table 1), it can be shown that the enthalpies of reactions (3) and (4) are only 60 and 20 kJ mol$^{-1}$ respectively:

$$SiH_4^+ \rightarrow SiH_3^+ + H; \quad (3)$$

$$SiH_4^+ \rightarrow SiH_2^+ + H_2. \quad (4)$$

**Table 1.** Some properties of methane and silane.

| Parameter | $CH_4$ | $SiH_4$ |
|---|---|---|
| $\Delta H_f^0$, kJ mol$^{-1}$ | −70 [117] | 30 [117] |
| $D(H_3E-H)$, kJ mol$^{-1}$ | 430 [117] | 350–400 [118] |
| $Ip(EH_4)$, kJ mol$^{-1}$ | 1220 [117] | 1130 [119] |
| $Ap(EH_3^+/EH_4)$, kJ mol$^{-1}$ | 1380 [117] | 1190 [118] |
| $Ap(EH_2^+/EH_4)$, kJ mol$^{-1}$ | 1470 [117] | 1150 [118] |
| $\mu$, D | +0.4 [121] | −1.6 [120] |

Notation: $\Delta H_f^0$ is the standard enthalpy of formation, $D(H_3E-H)$ the dissociation energy of the $H_3E-H$ bond, $Ip$ the ionisation potential, $Ap$ the appearance potential, and $\mu$ the dipole moment.
Note. The numbers in square brackets denote references (Ed.of Translation).

The enthalpies of the corresponding processes involving methane are 150 and 240 kJ mol$^{-1}$. Hence it follows that the $SiH_4^+$ ion, formed from the silane molecule, cannot be stable, bearing in mind the Franck–Condon principle, relative to the $SiH_3^+$ and $SiH_2^+$ ion and its peak is therefore absent from the mass spectrum of silane.

The principal ion in the system considered is $SiH_3^+$,[89–91] which is the product and reactant ion simultaneously:

$$SiH^+ + SiH_4 \rightarrow SiH_2 + SiH_3^+;$$
$$SiH_2^+ + SiH_4 \rightarrow SiH_3 + SiH_3^+;$$
$$SiH_3^+ + SiH_4 \rightarrow SiH_4 + SiH_3^+.$$

It is noteworthy that the $H_3Si^+$ ion was believed for a long time to be insufficiently active,[90] since a sharp rise was observed along the initial section of the curve relating the intensities of the peaks of this ion in the mass spectrum to the pressure (Fig.1). This finding showed that the rate of reaction of the $SiH_3^+$ ion in the region of low pressures is much lower than the rate of its formation. However, further investigation of the behaviour of this ion demonstrated that it is extremely active.[91] The point is that the main reaction of this ion involves the transfer to the hydride ion from silane, which results in the appearance of the same silyl cation. In order to elucidate the mechanism of this hydride transfer, the kinetic energy of the product ion was analysed using the deuteriated silane $SiD_4$ as the substrate.[91] The results of the analysis showed that the hydride ion transfer reaction proceeds mainly via the direct stripping mechanism.

However, there are also processes proceeding via a mechanism involving the formation of a long-lived complex, which is indicated by the presence of isotopically mixed

products:[91]

$$SiH_3^+ + SiD_4 \rightarrow [Si_2H_3D_4]^+ \begin{cases} \rightarrow SiD_3^+ + SiH_3D; \\ \rightarrow SiD_2H^+ + SiH_2D_2; \\ \rightarrow SiDH_2^+ + SiHD_3; \\ \rightarrow SiH_3^+ + SiD_4. \end{cases}$$

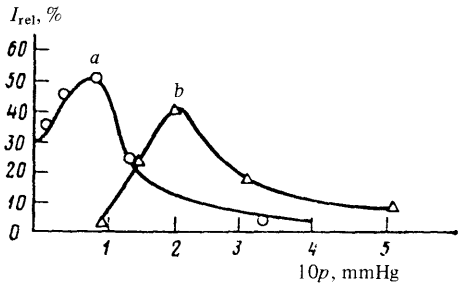



**Figure 1.** Dependence of the peak intensities of the $SiH_3^+$ (*a*) and $Si_2H_7^+$ (*b*) ions on pressure.[90]

Mass-spectrometric studies of the processes occurring in ionised methylsilane have been carried out in order to elucidate the role of the substituent (the methyl group).[92,93] One of the main ions (24%) formed on bombardment of methylsilane is $MeSiH_2^+$.[93] A characteristic reaction of this ion in methylsilane involves the abstraction of a hydride ion, as for unsubstituted silicenium ions. When the deuteriated methylsilane $MeSiD_3$ was used, it was shown that a hydride ion is abstracted from a Si–H bond and not from a C–H bond:[93]

$$MeSiH_2^+ + MeSiD_3 \rightarrow MeSiH_2D + MeSiD_2^+.$$

This is apparently due to the fact that the hydrogen in the Si–H bond is of the hydride type, while that in the C–H bond is of the proton type. The isotope distribution in the product ions shows that, as for silane, hydride transfer takes place mainly via the stripping mechanism; however, for low collision energies, processes involving the formation of a long-lived complex also take place.[93,123]

A mass-spectrometric study of $MeSiD_3$ showed that the hydrogen atoms in the methyl group are not involved in the hydrogen redistribution between the interacting species in the complex.[93]

Thus the C–H bonds are not involved in the hydride transfer reaction in silanes which proceed both via the direct mechanism and via the mechanism in which a long-lived complex is produced.

(*b*) *Ion–molecule reactions in silane–hydrocarbon mixtures.* Mass-spectrometric study of an ionised silane–hydrocarbon mixture is of great interest, because it becomes possible to follow simultaneously the ion–molecule reactions of silicenium and carbenium ions and to compare their chemical behaviour.

Processes in a silane–methane mixture have been investigated mass-spectrometrically in a number of studies.[94–96] The dominant processes in this system are the formation reactions of the $H_3Si^+$ ion via the mechanisms

$$CH_n^+ + SiH_4 \rightarrow CH_{n+1} + SiH_3^+, \text{ where } n = 0, 1, 2, 3; \quad (5)$$

$$CH_m^+ + SiH_4 \rightarrow CH_{m-1} + H_2 + SiH_3^+, \text{ where } m = 4, 5. \quad (6)$$

It has been shown[123] that the $C_2H_5^+$ ion, which is the main product of the ion–molecule reactions in methane, also reacts with silane to form exclusively the $SiH_3^+$ ion.

The possibility of the formation of the $SiH_3^+$ ion via proton transfer to the silane, postulated initially by some workers,[124] i.e.

$$CH_4^+ + SiH_4 \rightarrow [SiH_5^+]^* + CH_3 \rightarrow SiH_3^+ + H_2;$$
$$CH_5^+ + SiH_4 \rightarrow [SiH_5^+]^* + CH_4 \rightarrow SiH_3^+ + H_2.$$

is ruled out because the $SiH_5^+$ ion has not been detected even at a pressure of 0.5 mmHg.[96] If these processes did take place, one might have detected the $SiH_5$ ion stabilised by collisions at high pressure. The absence of the above proton transfer has been confirmed also by experiments carried out with fully deuteriated methane $CD_4$.[95] Within the limits of experimental error, the only silicenium ions in the mass spectrum are the $SiH_3^+$ ions.

We shall consider the reactions occurring in the silane–ethylene mixture. The main reactions in this case are also those involving the transfer of a hydride ion from silane to the attacking cation, which results in the formation of the $SiH_3^+$ ion:[7,97,125]

$$SiH_4 + C_2H_2^+ \rightarrow SiH_3^+ + C_2H_3;$$
$$SiH_4 + C_2H_3^+ \rightarrow SiH_3^+ + C_2H_4;$$
$$SiH_4 + C_2H_4^+ \rightarrow SiH_3^+ + Et.$$

In its turn, the silyl cation interacts with ethylene to form the complex $SiC_2H_7^+$, which is stabilised by collisions at high pressure. In the absence of stabilisation, this complex decomposes into the initial reactants or reaction products. Thus the interaction of the silyl cation with ethylene can be represented by means of the following schemes:

$$SiH_3^+ + C_2H_4 \rightarrow [SiC_2H_7^+]^* \rightarrow SiH_3^+ + C_2H_4;$$
$$[SiC_2H_7^+]^* \begin{cases} \rightarrow SiC_2H_5^+ + H_2; \\ \rightarrow SiCH_3^+ + CH_4; \\ \rightarrow SiC_2H_3^+ + 2H_2; \end{cases}$$
$$[SiC_2H_7^+]^* + C_2H_4 \rightarrow [SiC_2H_7^+] + C_2H_4^*.$$

A study[77] has shown that the majority of the collisions between the $SiH_3^+$ ion and the $C_2H_4$ molecule lead to the initial reactants. This can probably be accounted for by the fact that there exists a potential barrier separating the $H_3SiCH_2.CH_2^+$ ions formed initially from the more stable isomeric form $EtSiH_2^+$. The majority of the $H_3SiCH_2CH_2^+$ ions decompose rapidly into the reactants and only a small proportion isomerise to the $EtSiH_2^+$ ions. These ions and their dissociation products are in fact detected mass-spectrometrically. The maximum energy transmitted by the complex $EtSiH_2^+$ to the ethylene molecule on stabilisation by collision has been determined as 0.6–0.8 eV.[77] This is in good agreement with the results of a study[126] where it has been reported that the ethylene molecule is capable of accepting an excitation energy up to 1.3 eV without decomposition on collision within the excited species.

We shall now consider the ion–molecule reactions in the silane–benzene mixture.[99,100] The main product ions in this system as as follows; $C_6H_6^+$ (*m/e* 78), $SiC_6H_7^+$ (*m/e* 107), and $SiC_6H_9^+$ (*m/e* 109). It has been shown that the $SiC_6H_9^+$ ion is a long-lived complex with a lifespan of $10^{-5}$ s. At a high pressure this complex is stabilised by collisions, while in

the absence of stabilisation it decomposes into the reaction products $C_6H_6^+$ and $SiC_6H_7^+$. One can therefore put forward the following mechanism of the interaction of the silyl cation with benzene:

$$SiH_3^+ + C_6H_6 \rightarrow [SiC_6H_9^+]^*;$$

$$[SiC_6H_9^+]^* \begin{cases} \rightarrow C_6H_6^+ + SiH_3; \\ \rightarrow SiC_6H_7^+ + H_2; \end{cases}$$

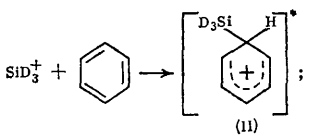
$$[SiC_6H_9^+]^* + C_6H_6 \rightarrow [SiC_6H_9^+] + C_6H_6^*.$$

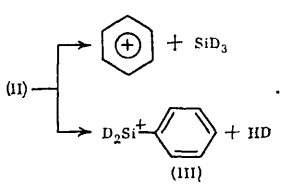
With increase of the kinetic energy of the reactant ion, the yield of the energy-enriched complex $SiC_6H_9^+$ falls sharply, while the relative yield of the product $SiC_6H_7^+$ falls much more slowly and the yield of the $C_6H_6^+$ ion increases sharply, reaching 70%. The unimolecular decomposition of the long-lived complex $[SiC_6H_9^+]^*$ also involves the formation of other ionic products in insignificant yields ($C_6H_7^+$, $SiC_4H_5^+$, and $SiC_4H_7^+$). Among these product ions, the $C_6H_7^+$ ion which is believed[100] to be formed on proton transfer from the silyl cation to benzene via the mechanism

$$SiH_3^+ + C_6H_6 \rightarrow C_6H_7^+ + SiH_2.$$

is of greatest interest. Analogous processes have been observed in the interaction of methyl cations with certain aromatic hydrocarbons, for example, with toluene.[127]

Experiments using fully deuteriated silane have shown[100] that the $SiD_3^+$ ion in the $SiC_6H_9^+$ complex retains its individuality and there is virtually no exchange of the hydrogen and deuterium ions in the complex. This permits the conclusion that the short-lived complex is an ion with a structure analogous to that of the σ-complex (II) and not an ion of the troplyium type. The interaction of the silyl cation $SiD_3^+$ with benzene can then be formulated schematically in the following manner:




The structure of the benzyl type (III) had already been proposed earlier in a study of the ionisation of phenylsilane by electron impact.[128]

The interaction of the methyl, ethyl, and butyl cations with methylsilanes having the general formula $Me_nSiH_{4-n}$, where $n$ = 0, 1, 2, 3, or 4, has been reported.[101-103] The characteristic reactions of the above carbenium ions with methylsilanes are reactions involving hydride transfer from the silane to the attacking ion with formation of a tervalent silicenium ion $Me_nSi^+H_{3-n}$ and also processes involving the abstraction of the methyl anion from the silane and its transfer to the carbenium ion with formation of the $Me_{n-1}Si^+H_{4-n}$ ion.

The probabilities that the hydride ion or the methyl anion are split off are not the same for different carbenium ions.[103] The probabilities that the methyl and ethyl cations are split off are almost the same. In the case of the propyl cations the transfer of the methyl anion begins only in the presence of three methyl groups, while for the butyl cations four methyl groups are needed in the silane molecule.

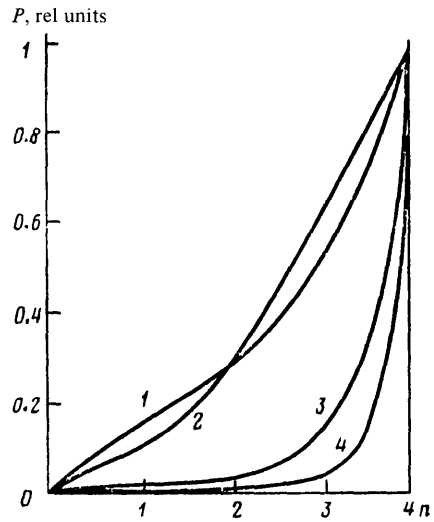



**Figure 2.** Dependence of the relative probability $P$ of the transfer of the methyl anion on the number of methyl groups $n$ in the methylsilane for different carbenium ions: *1*) $CH_3^+$; *2*) $C_2H_5^+$; *3*) $C_3H_7^+$; *4*) $C_4H_9^+$.[103]

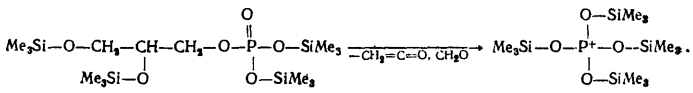
Fig. 2 illustrates the relative probabilities of the transfer of the $CH_3^-$ ion from the silane $Me_nSiH_{4-n}$ by various cations. The observed differences in the behaviour of the cations have been explained[103] by the fact that the propyl and butyl cations have the iso-structure. This hypothesis is consistent with the report[129] that the ionisation of neopentane by electron impact involves mainly the formation of the $Me_3C^+$ cation. Otherwise the propyl and butyl cations would have behaved in the same way as the ethyl cation.

The reactions of the methyl and ethyl cations with ethylsilanes of the type $Et_nSiH_{4-n}$, where $n$ = 0, 1, 2, 3, or 4, were investigated and it was shown that the transfer of an alkyl anion is not observed in methylsilane systems only.[102,103]

The studies considered have shown that it is possible to obtain three silicenium ions in a rarefied gaseous phase from the corresponding silanes with the aid of electron impact and by the interaction of various carbenium ions with silanes.

(c) *The ion–molecule reactions of trimethylsilicenium ions.* The next stage in the study of silicenium ions involved the investigation of the reactions of trimethylsilicenium ions with organic and organosilicon compounds belonging to various classes. An important step in this research consisted of studies devoted to questions concerning the rearrangement of the silicenium ions themselves.[40,104-110] The majority of such rearrangements can be accounted for by the localisation of the positive charge on the silicon atom and by the subsequent formation of a bond between

silicon and the electronegative centre, usually the oxygen atom:[104–110]

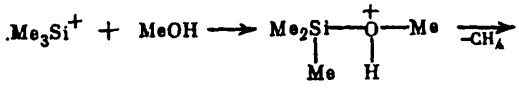


Apart from the peaks of the ions arising as a result of the intermolecular rearrangements, the presence of the (M + 73)† peak is characteristic of the spectra of all trimethylsilyl derivatives of organic compounds.[104–110] It has therefore been postulated[104–110] that an ion of this kind is formed as a result of the ion–molecule interaction of the trimethylsilicenium ion with the electronegative centre of the substrate molecule. These studies initiated the research into the ion–molecule reactions of trimethylsilicenium ions.

The interaction of trimethylsilicenium ions with a series of organic compounds containing various functional groups (indenamine, naphthaline, quinoline, octadec-1-ene) has been studied.[111,112] The main peak in the mass spectra of these compounds was that corresponding to the (M + 73) ion.

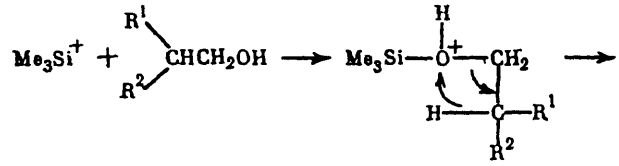
The investigations[111,112] established that trimethylsilicenium ions are extremely reactive species with very pronounced electrophilic properties owing to the presence of the positive charge, the unoccupied molecular *p* orbital, and the unoccupied *d* orbital. Despite the high reactivity of silicenium ions, a characteristic feature of the latter is the formation of the quasi-molecular (M + 73) complexes[111,112] and not fragment ions of the kind observed in the case of the carbenium ions. Thus the interaction of trimethylsilicenium ions with higher alcohols leads to the formation of quasi-molecular ions in 75% yield.[111] When trimethylcarbenium ions react with these alcohols, the total ionic current consists of the ionic currents of a multiplicity of fragment and quasi-molecular ions, the contribution of the quasi-molecular ion being insignificant.[130]

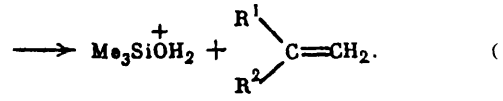
The investigation by the ion–cyclotron resonance method of the interaction of trimethylsilicenium ions with the alcohols ROH, where R = Me, Et, n-Pr, t-Bu, and other alkyl groups, has been reported.[113,114] It has been shown that the interaction of the silicenium ion with an alcohol molecule entails the formation of the adduct $\overset{+}{R}OH-SiMe_3$, which can then decompose further with loss of methane in the case of methanol and with loss of an alkene in the case of the remaining alcohols in accordance with the mechanism#





(7a)

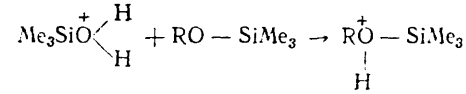




(7b)

The elimination of methane in accordance with the mechanism (7a) is insignificant for higher alcohols. The explanation is apparently the stability of the alkene, which renders the process involving the elimination of the alkene rather than the methane more favourable.

It has been shown[112] that steric effects play an important role in the ion–molecule reactions in the gas phase. The (M + 73) peak was almost absent from the spectra of compounds containing a secondary siloxy-group with bulky substituents. Instead their mass spectra contained an intense (M + 1) peak. The formation of this ion can be accounted for by the interaction of the trimethylsilicenium ion with the water (atmospheric moisture) present in the system; this entails the appearance of a protonated silanol $Me_3Si\overset{+}{O}H_2$, which reacts further with a substrate molecule as a Brønsted acid, giving rise to the (M + 1) ion:



This mechanism has been confirmed by experiments using deuteriated water. In this case the (M + 1) peak shifts by unity. In addition, a peak corresponding to the protonated silanol (*m/e* 91) was present in the spectrum.

Thus, under conditions where the interaction of the fairly large trimethylsilicenium ion with electronegative atoms is hindered, the process involving the formation of the (M + 1) ion, i.e. the protonation of the substrate molecules, becomes energetically more favourable. In those cases where there is no steric hindrance in the molecule, the main reaction of the trimethylsilicenium ion is the formation of the (M + 73) quasi-molecular ion.

It follows from the analysis of data examined that, in contrast to the condensed phase, in the gas phase silicenium ions are formed readily and the relative intensities of their peaks in the mass spectra exceed by 1–2 orders of magnitude the intensities of the carbenium ions formed under analogous conditions, which agrees with the lower formation energies of the silicenium ions.

Like carbenium ions, silicenium ions have fairly pronounced electrophilic properties. The results of studies of the gas-phase ion–molecule reactions of ions of both types have demonstrated a considerable analogy in the character of their interactions and of the products formed. At the same time, by virtue of the difference between the electronic structures and properties of the carbon and silicon atoms, some differences have also been observed in the behaviour of these ions.

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†The mass of 73 corresponds to that of the trimethylsilicenium ion.

#A radiochemical study of the gas-phase reactions of dimethylsilicenium ions with methanol at a vapour pressure of the latter of 30 mmHg and that of a noble gas diluent of ~300 mmHg have shown that the only product is dimethylmethoxysilane, which is formed as a result of the proton transfer from the long-lived complex to the alcohol molecule or to the diluent gas species.[131]

## IV. A NUCLEAR-CHEMICAL METHOD FOR THE GENERATION OF SILICENIUM IONS AND THE STUDY OF THEIR REACTIONS

The traditional physicochemical methods proved to be unsuitable for the generation of silicenium ions in either condensed or gas phases. The mass-spectrometric and ion-cyclotron resonance spectroscopic methods make it possible to obtain these ions and to investigate their reactions but only in the rarefied gas phase. A method which permits the investigation of silicenium ions in the gas phase over a wide range of pressures and also in the liquid and solid phases has recently become available. It is based on a combination of nuclear and chemical processes: the β-decomposition of the tritium atoms forming part of the composition of the silane molecule takes place initially and this is followed by chemical changes leading to the formation of silicenium ions.

In order to understand the essential feature of the method, it is necessary to consider the β-transformation of tritium. The β-decomposition process is known to involve the transformation of a neutron into a proton in the nucleus[132] via the mechanism

$$n \rightarrow p + e^- + \tilde{\nu},$$

where n and p are the neutron and proton respectively, $e^-$ is the nuclear electron (β-particle), and $\tilde{\nu}$ is the antineutrino. This transformation leads to the appearance of the nucleus of a new element with a charge greater by unity. Since the number of electrons in the atom remains unchanged in this process, the charge state of the resulting daughter element has increased by unity. Thus the β-decomposition of tritium can be represented schematically as follows:

$$T \rightarrow H^+ + e^- + \tilde{\nu}.$$

Since the β-particle is emitted over a period which is insignificant compared with the period of electronic vibrations, a sudden change under these conditions of the electric field of the nucleus can lead to the so-called "shaking" of the electron shell, which entails the excitation of the daughter ion.[133] In conformity with the sudden perturbation theory, this process should lead to the additional ionisation of some of the daughter ions.[134] However, for tritium, both the experimental data and calculations have shown that only 2.5% of all the transitions lead to the formation of doubly charged ions, i.e. ions with an excitation energy exceeding the second ionisation potential of helium. This is associated with a very marked intensification of the electrostatic interaction of the electron with the nucleus as a result of the doubling of the charge of the latter. Furthermore, the usual mechanism of the formation of multiply charged ions as a consequence of Auger processes does not obtain in the case of hydrogen (tritium).

The fact that the radioactive recoil energy,[133] which can also be responsible for the excitation of the ions formed, is insignificant is likewise characteristic of β-decomposition. Thus more than 90% of all the β-transformations of tritium are accompanied by a recoil energy less than 2 eV.

Thus, as a result of the β-decomposition of tritium, the yield of singly charged helium ions is a maximum compared with the yields of the ions of other elements and reaches ~97%; most of the singly charged ions (~70%) are then in the ground electronic levels or levels close to them.[134]

We shall now consider the processes occurring on decomposition of the tritium forming part of the composition of molecular systems, because these processes constitute the basis of the generation of reactive species, in particular carbenium ions.[135,136]

The first stage in the chemical changes in the β-decomposition processes of tritium atoms forming part of hydrocarbons is the appearance of primary molecular ions $RHe^+$. The results of theoretical and experimental studies[137–141] have shown that, as for atomic systems, most of the molecular ions formed are in the ground energy state or states close to it.

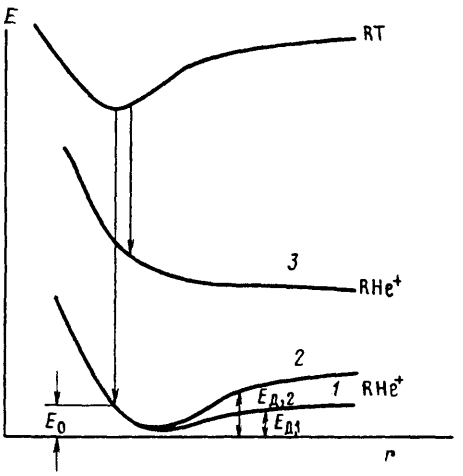



**Figure 3.** Potential energy curves for the RT molecule and the $RHe^+$ ion: *1*) and *2*) the ground state; *3*) the excited state.[140]

The configuration of the nuclei in the resulting molecular ion, which is characteristic of the initial molecular system, does not in general correspond to the minimum on the potential energy surface of this ion. According to the Franck–Condon principle, this means that the so-called vertical transitions on the potential energy diagram, associated with the change in the chemical nature and electronic state of the atoms, lead to the appearance of molecular ions in various vibrational levels. The potential energy curves for the initial molecule and the daughter ion are illustrated schematically in Fig. 3. Evidently, there can be two types of potential energy curves for the daughter ions in the ground states. In the first case the excitation energy $E_0$ is higher than the dissociation energy of the $RHe^+$ ion (curve *1*), while in the second case $E_0$ is lower than the dissociation energy of the $RHe^+$ ion (curve *2*). The first case leads to the decomposition of the primary molecular ion $RHe^+ \rightarrow R^+ + He^0$, while the second involves the retention of the $RHe^+$ ion.

Apart from the transitions leading to the ground states of the daughter ions, there can also be transitions resulting in excited states (curve *3*). In this case the potential energy curve has no minimum, which corresponds to a repulsion state. Such transitions inevitably lead to the dissociation of $RHe^+$ with formation of the $R^+$ ion. It has been shown[139,142,143] that the ions $R^+$ in the ground state do not undergo subsequent fragmentation.

The sequence of the processes developing in the β-decomposition of tritium forming part of hydrocarbons (for methane as an example) and their time characteristics have been

represented schematically as follows:

$$T_3C{:}T \xrightarrow[\sim 10^{-21}\,s]{\beta\,(a)} [T_3C{:}He^+,\beta] \xrightarrow[\sim 10^{-18}\,s]{(b)} \underset{(A)}{[T_3C{\cdot}He^+]} \xrightarrow[\sim 10^{-16}\,s]{(c)} \underset{(B)}{\rightarrow}$$

$$\rightarrow [T_3C{\cdot}He^+{\cdot}] \xrightarrow[\sim 10^{-15}\,s]{(d)} \underset{(C)}{[T_2C^+He{:}]} \xrightarrow[\sim 10^{-13}\,s]{(e)} \underset{(D)}{T_3C^+} + \underset{(E)}{He^0}.$$

Stage (*a*) is the transformation of the tritium nucleus into the helium nucleus, whereupon the β-particle is within the limits of the helium atom. In stage (*b*) the β-particle lies outside the limits of the molecular system, which entails the appearance of a positively charged molecular ion (B) in which the charge is localised on the helium atom. Stage (*c*) corresponds to the intra-atomic transition of the residual electron left over from the tritium atom to the energy level of the helium atom corresponding to its second ionisation potential. Stage (*d*) is the interatomic transition of an electron from the carbon atom to the helium atom—to the energy level corresponding to the first ionisation potential of this atom. The electron transfer from the hydrocarbon group to the helium atom is caused by the fact that the first ionisation potential of helium greatly exceeds (by ~15 eV) the ionisation potentials of the hydrocarbon groups. In the resulting molecular ion (D) the neutral helium atom and the charged $R_3C^+$ fragment become isolated. Stage (*e*) involves their separation in space, which leads to the formation of free carbenium ions. The yields of the carbenium ions obtained in this way are ~80%.[137,144]

Table 2. The probabilities *P* of the appearance of the daughter species in the ground state in the β-decomposition of a tritium atom in certain compounds.[138]

| Process | *P* |
|---|---|
| $T \xrightarrow{\beta^-} He^+$ | 0.70 |
| $HT \xrightarrow{\beta^-} HHe^+$ | 0.59 |
| $CH_3T \xrightarrow{\beta^-} CH_3He^+$ | 0.61 |
| $NH_2T \xrightarrow{\beta^-} NH_2He^+$ | 0.61 |
| $OHT \xrightarrow{\beta^-} OHHe^+$ | 0.62 |

Quantum-chemical calculations[138] have shown that the nature of the initial parent form in the β-decomposition of tritium atoms does not have a significant influence on the probability of the appearance of the daughter species in the ground energy state (Table 2). It is therefore to be expected that the β-decomposition processes involving the tritium atom in the corresponding compounds of the elements in the Third Period lead to the formation of primary molecular ions whose yield in the ground energy state is close to the yield of the ions indicated in Table 2. Thus, when the tritium forming part of the composition of organosilicon compounds, in particular the substituted silanes $R_{4-n}SiT_n$, decomposes, silicenium ions in the ground energy state are formed in fairly large yields in accordance with the scheme

$$R_{4-n}SiT_n \xrightarrow{\beta} R_{4-n}Si^+T_{n-1} + He^0.$$

Thus a possibility is created for extending the nuclear-chemical method for the generation of free carbenium ions to the preparation of their silicon analogues (silicenium ions). This method of generation of silicenium ions has a number of characteristic features.

1. The silicenium ions generated by the nuclear-chemical method are formed in a free state, i.e. without a counterion and a solvation shell. The β-particle emitted on decomposition cannot serve as a counterion, because it is removed to a distance over which the interaction energy between the ion and the electron is low. The absence of a solvation shell is explained by the fact that the initial molecular system lacked such a shell and the time required for its creation after the formation of the ion exceeds by several orders of magnitude the time of the ion–molecule interactions. Such a state of the ions formed ensures their enhanced reactivity.

2. The method makes it possible to obtain, in principle, silicenium ions with the required composition and structure and with a specific localisation of the charge, because organosilicon compounds having the corresponding structure and containing tritium in the specified position can be used as the sources of such ions.

3. The rate of generation of the silicenium ions (E) is independent of external conditions (temperature, pressure, the state of aggregation, etc.), because the formation of these ions is based on radioactive decomposition processes:

$$\frac{dN(R_{4-n}Si^+T_{n-1})}{dt} = n\lambda K N(R_{4-n}SiT_n),$$

where $N(R_{4-n}Si^+T_{n-1})$ is the number of silicenium ions formed, $N(R_{4-n}SiT_n)$ the number of silane molecules, $\lambda$ the decomposition constant of tritium, *n* the number of tritium atoms in the silane, and *K* a coefficient taking into account the yield of silicenium ions.

4. The given method makes it possible to generate silicenium ions and to investigate their reactions in the gas, liquid, and solid phases, since the β-decomposition processes are independent of the state of aggregation of the substance in the molecules of which tritium decomposes.

Dimethylsilicenium ions were obtained for the first time with the aid of the nuclear-chemical method via the process

$$Me_2SiT_2 \xrightarrow{\beta} [Me_2SiTHe]^+ \rightarrow Me_2SiT^+ + He^0$$

and their reactions with t-butoxydimethylsilane, pentadimethyldisiloxane, and methanol were investigated by Nefedov et al.[131] The reactions of the dimethylsilicenium ions with the compounds enumerated above are indicated schematically below:

$$\left[\begin{matrix} Me_2HSi^{\delta+}\ldots OR \\ | \\ Me_2TSi \end{matrix}\right] \rightarrow Me_2HSi^+ + Me_2TSiOR$$

$$\uparrow$$

$$Me_2TSi^+ + Me_2HSiOR \rightarrow \left[\begin{matrix} Me_2HSi\overset{+}{O}R \\ \vdots \\ Me_2TSi \end{matrix}\right]^* \rightarrow \left[\begin{matrix} Me_2HSiO\ldots R^{\delta+} \\ | \\ Me_2TSi \end{matrix}\right] \rightarrow Me_2HSiOSiTMe_2 + R^+;$$

$$Me_2TSi^+ + MeOH \rightarrow \left[\begin{matrix} Me\overset{+}{O}H \\ \vdots \\ Me_2TSi \end{matrix}\right]^* \xrightarrow{MeOH} Me_2TSiOMe + Me\overset{+}{O}H_2;$$

$R = Me_3C,\ Me_3Si.$

Further studies in this field should probably be directed to the extension of the nuclear-chemical method to the generation of other silicenium ions and to the study of their reactions with compounds of different classes in the gas and condensed phases.

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In conclusion one must state that the problem of the preparation of silicenium ions and of the investigation of their properties and reactions still remains in the stage of

development. One of the directions of this development involves the use of the nuclear-chemical method. The above discussion of the essential features of this method and of its characteristic features permits the conclusion that the method is unique, because it allows one to generate silicenium ions of different composition and structure in any substances in the gas, liquid, and solid states. The development of this method will make it possible to investigate the behaviour of silicenium ions in reactions with compounds of different classes both in the gas phase, over a wide range of pressures, and in the condensed phases.

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# Chalcogeniron Carbonyl Clusters

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The literature data and the methods of synthesis, structure, and physicochemical properties of chalcogeniron carbonyl clusters and their derivatives are surveyed and described systematically.
The bibliography includes 163 references.

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## I. INTRODUCTION

Iron clusters are particularly abundant among transition metal carbonyl complexes with sulphur-containing ligands.[1] Typical representatives of chalcogeniron carbonyl clusters are dichalcogendiiron hexacarbonyl $(\mu\text{-}X)_2Fe_2(CO)_6$ (I) and dichalcogentriiron nonacarbonyl $(\mu_3\text{-}X)_2Fe_3(CO)_9$ (II), where X = S, Se, or Te [for brevity, the formulae used subsequently will be $X_2Fe_2(CO)_6$ and $X_2Fe_3(CO)_9$].

The chemistry of these clusters has so far developed extensively, but some of their features have not been adequately explained. The study of the methods of synthesis and the properties of clusters (I) and (II) under comparable conditions involves considerable experimental difficulties. Very few thoroughly developed methods of synthesis of the above cluster compounds are so far available. Their chemical properties have likewise not been studied systematically.

Chalcogeniron carbonyl complexes, which are the compounds of a large number of cluster derivatives, in particular the cubane systems $[S_4Fe_4(SR_4)]^{n-}$, themselves possess a series of unique properties, which are considered in the present review. For example, sulphur-containing iron clusters enter into the composition of polynuclear enzymes (ferredoxins)—a new class of biocatalysts which play an exceptional role in vitally important processes such as the fixation of molecular nitrogen. The chemical modelling of the catalytic properties of cluster enzymes will make it possible to create fundamentally new effective catalysts of many industrial processes.

The aim of the present review is a critical consideration of the methods of synthesis and the structure of chalcogeniron carbonyl clusters together with the discussion of their physicochemical properties. Although more than 150 communications have been published on this subject, so far no attempt has been made to survey them and to give a systematic account. We believe that a review of the methods of synthesis and chemical properties of chalcogeniron carbonyl clusters is extremely urgently required in connection with the vigorous development of a new scientific discipline—the chemistry of cluster compounds.[2]

## II. METHODS OF SYNTHESIS

As already mentioned, there are as yet very few thoroughly developed methods of synthesis of chalcogeniron carbonyl clusters. The majority of these clusters have been obtained non-specifically. The interaction of aqueous alcoholic solutions of alkali metal tetracarbonylferrate salts with sulphurous acid (or selenous and tellurous acid respectively) must be regarded as the most general method whereby such compounds can be obtained. This method synthesis is so far the most convenient and the one most frequently used for preparative purposes. A survey of the methods of synthesis shows that molecules with different chemical properties can serve as sources for the preparation of the same chalcogeniron carbonyl clusters. Thus for sulphur these are compounds exhibiting differences from the standpoint of the formal valence of sulphur, such as $S_8$, $H_2S$, $SO_2$, $CS_2$, RSH, etc. These compounds will be considered below in greater detail as sources of sulphur.

Analysis of the literature data (see the Table below) has shown that the most effective methods of synthesis of iron carbonyl clusters involve the reaction of elemental sulphur $S_8$ [3] or hydrogen sulphide[4] with dodecacarbonyltriangulotriiron (DDCI) $Fe_3(CO)_{12}$. A novel method of synthesis of clusters of types (I) and (II), where X = S, based on the interaction of elemental sulphur with the triethylammonium salt of undecacarbonyltriiron hydride (TSUTH) $[(C_2H_5)_3NH]^+[HFe_3(CO)_{11}]^-$ is noteworthy.[3] Satisfactory results have also been obtained in the synthesis of the compound $S_2Fe_3(CO)_9$ from DDCI and 3-chloropropenyl sulphide[5] or by the reaction of $(C_6H_5)_3CSH$ with DDCI.[6] The reaction conditions and the method used to isolate the products apparently play a significant role in the synthesis of chalcogeniron carbonyl clusters.

We shall consider initially the method of synthesis of chalcogeniron carbonyl clusters in which a mixture of compounds (I) and (II) is formed.

### 1. Interaction of Elemental Sulphur and Hydrogen Sulphide with Iron Carbonyls

The compounds $X_2Fe_2(CO)_6$ and $X_2Fe_3(CO)_9$ where X = S, Se, or Te) can be regarded as the products of the substitution of the bridging carbonyl groups in $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ by chalcogens.[7]

Until recently, there has been no information in the literature about the direct interaction of sulphur, selenium, and tellurium with iron carbonyls. It has been reported only that iron pentacarbonyl (IPC) does not react with elemental sulphur in the cold in solutions in carbon tetrachloride and xylene.[8] It has been shown[9-11] that elemental sulphur reacts with iron pentacarbonyl, iron nonacarbonyl (INC), and iron dodecacarbonyl in solution in benzene in

the course of 1–2 h at 80 °C to form very small amounts (2–5%) of the sulphur-containing clusters $S_2Fe_2(CO)_6$ and $S_2Fe_3(CO)_9$ in proportions of 1 : 3.

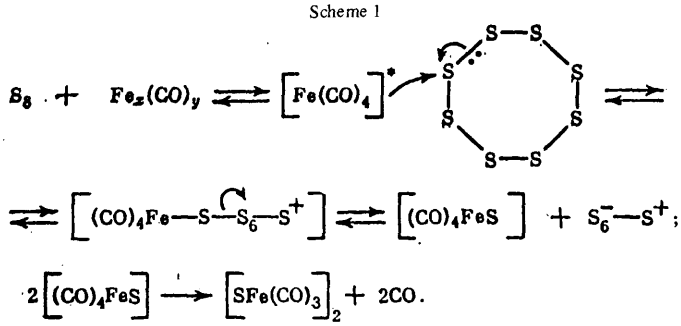
The reaction of elemental sulphur with iron carbonyls has been studied in greater detail by Mavlonov,[3] who examined the influence of the composition of the iron carbonyl, the reaction time, the reaction temperature, the reactant ratio, and the nature of the solvent and activating agents on the yield and ratio of compounds of types (I) and (II) and described the conditions for the chromatographic separation of these clusters.

The increase in reactivity of iron carbonyls in the sequence $Fe(CO)_5 < Fe_2(CO)_9 < Fe_3(CO)_{12}$ in the reaction with elemental sulphur agrees well with the hypothesis that the reactivity of iron carbonyls depends not only on the rate of formation and the amount of the coordination-unsaturated intermediate $[Fe(CO)_4]^*$ but also on the nuclearity of the cluster.[12–15]

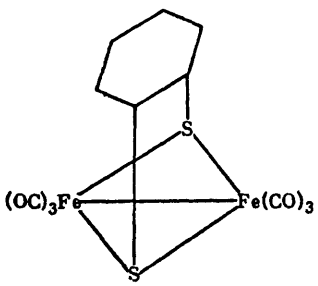
On the basis of available data on the interaction of sulphur compounds with iron carbonyls,[16–19] the reaction presumably proceeds via Scheme 1.

In certain cases where large amounts of the starting materials were used [0.075 mole of $S_8$ and 0.1 mole of $Fe_3(CO)_{12}$], it was possible to isolate in addition a further two substances in very small amounts.[3] One of these compounds is dithiodiiron heptacarbonyl $S_2Fe_2(CO)_7$ (III). It is a pale-orange crystalline substance with a melting point of 81–82 °C, which is readily soluble in organic solvents and is relatively stable in the solid state, while in solutions it is quantitatively converted on standing into $S_2Fe_2(CO)_6$ with evolution of CO.

Scheme 1



The structure of cluster (III) has been confirmed by elemental analysis, infrared spectroscopy, mass spectrometry, and X-ray diffraction.[20] The interaction of $Fe_3(CO)_{12}$ with a methanolic solution of NaOH and subsequent acidification of the solution in the presence of $Na_2SO_3$ yielded the cluster $SFe_3(CO)_{10}$ (IV).[21] At the same time the reaction of $S_8$ with an excess of cyclohexene or hex-1-ene in the presence of $Fe_3(CO)_{12}$ resulted in the formation,[22] apart from compound (IV), also of $S_2Fe_2(CO)_6$, $S_2Fe_3(CO)_9$, and the dithiolandiiron hexacarbonyl cluster having the structure



When cyclohexene is used, sulphur atoms are inserted in the double bond with formation of cyclic polysulphides. The structure of cluster (IV) has been studied by X-ray diffraction.[22]

The second compound formed together with compound (III) is apparently a polynuclear high-molecular-weight cluster $[S_xFe_y(CO)_z]$ (V), which is soluble only in polar organic solvents and is generated on heating compounds (I) or (II). The formation of a polynuclear cluster has also been noted in the interaction of elemental sulphur with dicobalt octacarbonyl.[23–25]

The methods of synthesis of clusters of types (I) and (II).

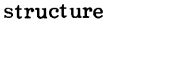
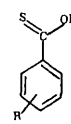
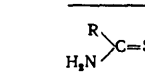
| Initial compounds | | Reaction conditions | Product (yield, %) | Refs. |
|---|---|---|---|---|
| sulphur compound | iron carbonyl | | | |
| $S_8$ | $Fe(CO)_5$ | $CCl_4$; $(CH_3)_2C_6H_4$; in the cold | — | [8] |
| $S_8$ | $Fe(CO)_5$; $Fe_2(CO)_9$; $Fe_3(CO)_{12}$ | $C_6H_6$; 80°; 1–2 h | (I):(II)=1:3 (2–5) | [9] |
| $S_8$ | $Fe_3(CO)_{12}$ | $C_6H_6$; 60°; 4 h | (I):(II)=4:1 (23.6) | [3] |
| $S_8$ | $Fe_3(CO)_{12}$ | THF; 60°; 6 h | (I)+(II); (36.7) | [3] |
| $H_2S$ | $Fe_3(CO)_{12}$ | $C_6H_6$; 52–54°, 2 h | (I):(II)=2:1 (90) | [4] |
| $S_8$ | $[(C_2H_5)_3NH]\times$ $\times[HFe_3(CO)_{11}]$ | $C_6H_6$; 60°; 6 h | (I):(II)=1:3 (33) | [3] |
| $H_2XO_3$; $Na_2S\times$ $\times 9H_2O$, X=S, Se, Te | $Fe(CO)_5$+$CH_3OH$+ +KOH | $H_2O$; 0° | (I)+(II) * | [32] |
|  | $Fe_3(CO)_{12}$ | $C_6H_6$; 80°; 4 h | (II) (10) | [5] |
|  | $Fe_3(CO)_{12}$ | $C_6H_6$; 80°; 4 h | (II) (55) | [5] |
| $SO_2$ | $Fe_2(CO)_9$ | petroleum ether; −10–−20°; 2 h | (II) ** | [41] |
| $S_4(H_{28}CC_6H_5)_2$ | $Fe_3(CO)_{12}$ | $C_6H_6$; 50°; 9 h | (II) | [16] |
|  | $Fe_2(CO_9)$ | $C_6H_{14}$; 70°; 3 h | (II) (19) | [43] |
| $F_3C-S-S-CF_3$ | $Fe_2(CO)_9$ | $C_6H_{14}$; 70° | (I) (0.3); (II) (0.1) | [47] |
| t-$C_4H_9SH$ | $Fe_3(CO)_{12}$ | $C_6H_6$; 80°; 12 h | (II) (10) | [49] |
| $(C_6H_5)_3CSH$ | $Fe_3(CO)_{12}$ | $CH_3C_6H_5$; 80°; 4 h | (II) (57) | [6] |
|  | $Fe(CO)_5$ | $C_6H_6$; 78–80°; 14 h | (II) (26.7) | [54] |
|  | $Fe_2(CO)_9$ | $C_6H_6$; room temp. | (II) (5.4–18.3) | [56,57] |
|  | $Fe_2(CO)_9$ | $C_6H_6$; room temp. | (II) (0.7–7.5) | [58,59] |
|  | $Fe_2(CO)_9$ | $C_6H_6$; room temp. | (II) (0.1–2.5) | [17] |

Table (contd.).

| Initial compounds | | Reaction conditions | Product (yield, %) | Refs. |
|---|---|---|---|---|
| sulphur compound | iron carbonyl | | | |
|  | $Fe_2(CO)_9$ | THF; room temp. | (II) (5.5) | [17,60] |
| Thiocamphenone | $Fe_2(CO)_9$ | — | (II) (1.9) | [61] |
| Thiofenchone | $Fe_2(CO)_9$ | — | (I) (4.57); (II) (15.7) | [61] |
| 2-Thiono-1,3-dioxolan-chromium pentacarbonyl | $Fe(CO)_5$ | THF | (II) ** | [62] |
| Diphenylthionocyclopropene | $Fe_2(CO)_9$ | THF | (II) ** | [63] |
| R—N=S—N—R | $Fe_2(CO)_9$ | $C_6H_{14}$ or $C_6H_6$; 70–80°; 2–3 days | (II (1.5) | [65,67] |
| $CS_2$ | $Fe_3(CO)_{12}$ | $C_6H_{14}$; 80°; 7.5 h | (II) ** | [68] |
| 1,3-dithiole-2-thione | $Fe_2(CO)_9$ | — | (II) (8.0) | [69] |

*The yield is not quoted.
**Traces.

A mixture of clusters of types (I) and (II) in proportions of 2:1 has been isolated in 90% yield on passing an excess of hydrogen sulphide through a benzene solution of DDCI (52–54 °C, 2 h):[4]

$$H_2S + Fe_3(CO)_{12} \rightarrow S_2Fe_2(CO)_6 + S_2Fe_3(CO)_9.$$

It has been shown that TSUTH, which is an intermediate in the synthesis of DDCI, can be used successfully to obtain sulphur-containing compounds of types (I) and (II) [yield 33%, $C_6H_6$, 6 h, 60 °C, ratio (I):(II) = 1:3].[3] This method can be of preparative value in view of the availability of IPC and the possibility of regenerating triethylamine whose reactivity is relatively low in the substitution of CO groups in the clusters obtained.

It is noteworthy that, when iron carbonyls react with elemental sulphur or hydrogen sulphide and also when TSUTH reacts with sulphur, the initial reaction product is, according to thin-layer chromatographic (TLC) data, dithiodiiron hexacarbonyl, which is subsequently converted into a compound of type (II):[3]

$$S_2Fe_2(CO)_6 \xrightarrow{Fe_2(CO)_{12}} S_2Fe_3(CO)_9.$$

In earlier studies it was reported that the reaction of DDCI with 2-mercaptobenzothiazole, thiosemicarbazide, thioacetamide, or parathioformaldehyde leads to the formation of the compound $(H_2C)S_2Fe_3(CO)_{10}$ [26] in a low yield. Later it was demonstrated that in reality this compound is dithiotriiron nonacarbonyl $S_2Fe_3(CO)_9$.[27]

Spongy iron and matte, granulated iron, and certain natural ores are used as the iron-containing raw material in the industrial preparation of IPC.[28] The iron matte consists of an alloy of iron (in the form of filings) and iron pyrite $FeS_2$ in proportions of 3:1. The alloy contains ~92% of iron and 8% of sulphur. A number of studies have been devoted to the influence of sulphur compounds on the formation of iron, molybdenum, and nickel compounds.[29–31]

In the development of preparative methods for the synthesis of IPC from the metal in the absence of solvents, it has been established that small amounts of sulphur or selenium have a favourable effect on the reaction.[29] A systematic investigation has therefore been made of the influence of added sulphur, selenium, and tellurium on the formation of IPC[7] and it was suggested that these elements act as catalysts, forming intermediate clusters such as $S_2Fe_3(CO)_9$, which subsequently decompose under the influence of carbon monoxide to form IPC and sulphur. It was shown that the formation of nickel carbonyl is appreciably accelerated under the influence of hydrogen sulphide.[31] The first intermediate formed in this process is nickel γ-sulphide, which is reformed in subsequent transformations together with segregation of $Ni(CO)_4$, and catalyses the reaction at very minute concentrations.

An interesting phenomenon, the activation of the formation of iron, molybdenum, and nickel carbonyls by friction in the presence of sulphur-containing substances, has been described.[31] According to the authors, friction causes the breakdown of the crystal lattices of iron and the metal sulphide and the reaction proceeds via the disproportionation of the carbonyl sulphide formed:

$$\text{iron} + \text{sulphur} \rightarrow \text{iron sulphide} \xrightarrow{CO} \rightarrow S_2Fe_3(CO)_9 \xrightarrow{\text{disproportionation}} \begin{cases} \rightarrow Fe(CO)_5 \\ \rightarrow \text{iron sulphide} \end{cases}.$$

The mechanism of iron carbonyl formation via a stage involving the appearance of the intermediate $S_2Fe_3(CO)_9$, which was described previously,[29] does not operate solely in a high-pressure reactor but also under the conditions of mechanical treatment.

Analysis of the literature data on the synthesis of IPC under various conditions from iron and carbon monoxide in the presence of small amounts of elemental sulphur has shown that in certain cases dithiotriiron nonacarbonyl, which is a catalyst of this reaction, is formed.[29–31]

Thus, as shown above, the interaction of elemental sulphur and hydrogen sulphide with iron carbonyls and TSUTH leads to the formation of a mixture of clusters (I) and (II) in satisfactory yields.

## 2. The Synthesis from Tetracarbonylferrates

Chalcogeniron carbonyls of type (II) were first obtained[32] by the interaction of aqueous alcoholic solutions of alkali metal tetracarbonylferrate salts with sulphurous acid (and similarly with selenous and tellurous acids):

$$3[Fe(CO)_4]^{2-} + 2XO_3^{2-} + 10H^+ \rightarrow X_2Fe_3(CO)_9 + CO_2 + 2CO + 5H_2O.$$

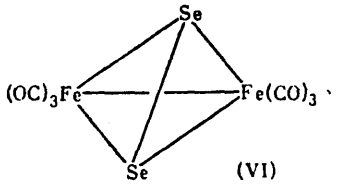
The reactions with $[Fe_2(CO)_8]^{2-}$ and $[Fe_3(CO)_{11}]^{2-}$ take place in the same way and in this case $Fe_3(CO)_{12}$ is formed as well. It is noteworthy that, as established subsequently, a mixture of compounds (I) and (II) is formed in all cases.[27–31,33]

Under analogous conditions, when the tetracarbonylferrate ion is acidified with hydrochloric acid, it reacts with sodium polysulphide to form a mixed precipitate of $S_2Fe_2(CO)_6$ and $S_2Fe_3(CO)_9$ [32] (these compounds can be separated by subliming the first *in vacuo* at 40 °C):

$$5[Fe(CO)_4]^{2-} + S_5^{2-} + 2H^+ \rightarrow S_2Fe_2(CO)_6 + S_2Fe_3(CO)_9 + H_2S + 5CO.$$

The cluster $Se_2Fe_2(CO)_6$ (VI) has also been obtained by treating with KOH a solution of $Fe(CO)_5$ in methanol at 0 °C in an atmosphere of $N_2$ with subsequent addition of selenium and then a solution of $Na_2Se.9H_2O$ in water, the reaction mixture being stirred for 1 h and then acidified with a 15% HCl solution.[32] The properties of cluster (VI) have been recently described in detail.[34]

The cluster $Se_2Fe_3(CO)_9$ (VII) has been synthesised analogously[32] and its structure has been determined[35] by X-ray diffraction:




(VI)

The clusters $Te_2Fe_3(CO)_9$ (VIII)[32,36] and $Te_2Fe_2(CO)_6$ (IX) have been obtained by adding $K_2TeO_3$ to a solution of $Fe(CO)_5$ and KOH in aqueous methanol with subsequent acidification of the reaction mixture with HCl. Under analogous conditions, IPC reacts with compounds (IX) to form $Te_2Fe_3(CO)_{10}$ (X), which the authors suggest[36] is an intermediate in the formation of compound (VIII). The reaction of $Fe(CO)_5$ with compound (IX) in the presence of $(CH_3)_3NO$ affords compound (VIII):

$$Te_2Fe_2(CO)_6 + Fe(CO)_5 + 2(CH_3)_3NO \rightarrow Te_2Fe_3(CO)_9 + 2CO_2 + 2(CH_3)_3N.$$

The structure of cluster (VIII) has been established by X-ray diffraction.[37]

Iron clusters containing two different chalcogen atoms in one molecule were first obtained from the tetracarbonylferrate ion.[38] Despite certain difficulties in the isolation of these substances (repeated thin-layer chromatography), the reaction is of practical interest, since it leads to the formation in one stage of clusters which are otherwise difficult to obtain:

$$[Fe(CO)_4]^{2-} + XO_3^{2-} + YO_3^{2-} + H^+ \rightarrow X_2Fe_3(CO)_9 + XYFe_3(CO)_9 + Y_2Fe_3(CO)_9 + CO_2 + CO + H_2O;$$
$$X \text{ и } Y = S, Se, Te;\ X \neq Y.$$

The compounds $XYFe_3(CO)_9$ are solid crystalline substances whose external appearance and properties are very similar to clusters of type (II), which are already known. They do not dissolve in water but do dissolve in organic solvents, namely aliphatic and aromatic hydrocarbons, ether, carbon tetrachloride, chloroform, and especially $CS_2$; they are stable in the solid state in air, while in solution they are also stable in an inert atmosphere but in air they decompose to form brown amorphous insoluble deposits.[38]

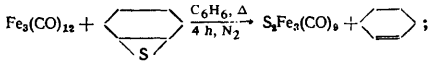
The formation of a cluster of type (II) in satisfactory yield by the reaction of the tetracarbonylferrate ion with sulphoxylic acid has been mentioned.[39]

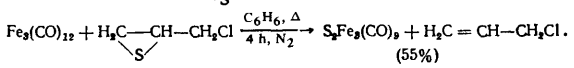
Thus the synthesis of a mixture of chalcogeniron carbonyl clusters (I) and (II) from aqueous alcoholic solutions of alkali metal tetracarbonylferrate salts and the corresponding acids must be regarded as the most general method of their synthesis.

We shall now consider the reactions of various organosulphur compounds with iron carbonyls which lead to the formation of the compound $S_2Fe_3(CO)_9$ as a side product.

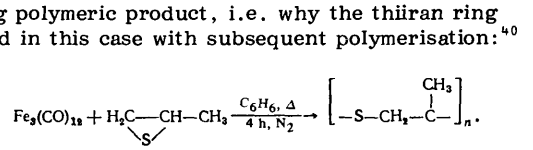
*(a) Reactions of cyclohexene sulphide and 3-chloropropene sulphide with DDCI.* The reaction of DDCI with cyclohexene or 3-chloropropene sulphide in boiling benzene involves the cleavage of the carbon–sulphur bond and the formation of a substance which was initially believed to be an isomer of $S_2Fe_3(CO)_9$.[5]

The decomposition of the thiiran ring with elimination of the sulphur atom and the formation of alkenes is a characteristic property of thiirans.[40] The method of synthesis of $S_2Fe_3(CO)_9$ from cyclohexene and 3-chloropropene sulphides is based on the desulphurisation of thiirans:[5]



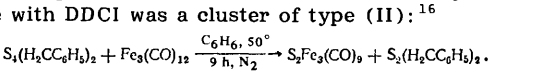




The conditions governing the elimination of sulphur in such cases are much milder compared with thermal desulphurisation, which indicates the preliminary coordination of DDCI or its decomposition products to the sulphur atom. At the same time it is not clear why the main product of the reaction of methylthiiran with $Fe_3(CO)_{12}$ is the corresponding polymeric product, i.e. why the thiiran ring is opened in this case with subsequent polymerisation:[40]



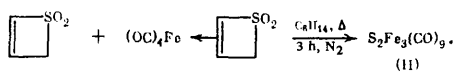

*(b) The reaction of sulphur dioxide, polysulphides, and thiacyclobutene sulphone with iron carbonyls.* The interaction of INC with sulphur dioxide in the absence of irradiation leads to $Fe_2(CO)_8SO_2$; a small amount of $S_2Fe_3(CO)_9$ was isolated together with the above product.[41] The reaction was carried out by passing $SO_2$ through petroleum ether containing a suspension of $Fe_2(CO)_9$ or in liquid $SO_2$ at −10° or −20 °C. However, Field and Newlands[42] did not detect $S_2Fe_3(CO)_9$ in the reaction product (−10 °C, inert atmosphere, 2 h); the reaction mixture contained $Fe_2(CO)_8SO_2$ and $Fe(CO)_5$. Analogous products have been isolated using DDCI.

One of the products of the interaction of bibenzyl tetrasulphide with DDCI was a cluster of type (II):[16]



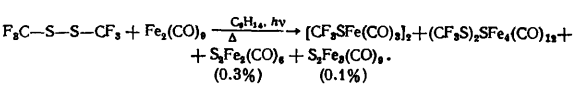

A suspension of 1,1-dioxothiacyclobuteneiron tetracarbonyl, obtained from thiocyclobutene sulphone and $Fe_2(CO)_9$, gives rise to cluster (II) in 19% yield on refluxing with thiacyclobutene sulphone in hexane[43] (Scheme 2). It is of interest to note that not even traces of $Fe_2(CO)_8SO_2$ and a compound of type (I) were detected in the reaction products.

Scheme 2




(II)

*(c) The reactions of thiols and disulphides with iron carbonyls.* It is well known that dialkyl sulphides, dialkyl disulphides, primary aliphatic thiols, and the corresponding aryl derivatives react with iron carbonyls to form bis(alkyl-, arylthioiron tricarbonyls) (bis-ATITC) having the general formula $[RSFe(CO)_3]_2$ (XI).[44–46] Only two cases where the sulphur atom was eliminated from disulphides and thiols have been described. Thus very small amounts of clusters of types (I) and (II) have been isolated on treating bis(trifluoromethyl) disulphide with $Fe_2(CO)_9$. The main product was the corresponding bis(trifluoromethylthioiron tricarbonyl).[47] Compounds (I) and (II) were not formed when $Fe(CO)_5$ was used:



A higher yield (10%) of compound (II) was achieved in the reaction of $Fe_3(CO)_{12}$ with secondary and tertiary aliphatic thiols:[48,49]

$$t\text{-}C_4H_9SH + Fe_3(CO)_{12} \xrightarrow[12\ h]{C_6H_6,\ \Delta} [t\text{-}C_4H_9SFe(CO)_3]_2 + (t\text{-}C_4H_9S)_3Fe_3(CO)_9 + (t\text{-}C_4H_9S)_2SFe_4(CO)_{12} + S_2Fe_3(CO)_9.$$

(35%) (5%) (5%) (10%)

Winter and co-workers[6,50–53] carried out a series of studies on the deprotonation and substitution reactions with trinuclear iron clusters $(RS)(H)Fe_3(CO)_9$ (XII) and $(\mu_3\text{-}X)(\mu_3\text{-}S)Fe_3(CO)_9$ (XIII), where X = PR, AsR, or SO. The compound $S_2Fe_3(CO)_9$ has been obtained in a high yield (57%) by the reaction of $Fe_3(CO)_{12}$ with RSH, where R = $C(C_6H_5)_3$ (toluene, 80 °C, 4 h) together with clusters (XII).[6]

On decomposition, bis(fluorocarbonyl)disulphane also acts as a source of elemental sulphur and gives rise to a cluster of type (II) on interaction with $Fe(CO)_5$:[54]

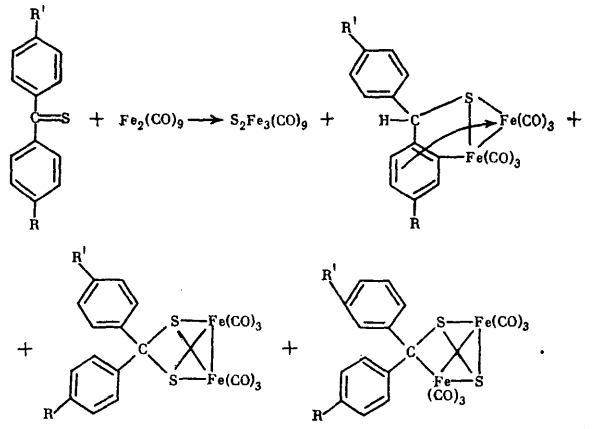
$$F\text{–}\overset{O}{\overset{\|}{C}}\text{–}S\text{–}S\text{–}\overset{O}{\overset{\|}{C}}\text{–}F + Fe(CO)_5 \xrightarrow[14\ h,\ Ar]{C_6H_6,\ 78\text{–}80^\circ} S_2Fe_3(CO)_9.$$

(26.7%)

A compound of type (II) has been detected when industrial pipes through which a mixture of carbon monoxide and methane had been passed for a long time under a high pressure were disassembled.[55] This cluster might have been formed with participation of sulphur compounds behaving as donors of atomic sulphur and present in the gas mixture as an impurity, via a stage involving the preliminary formation of iron carbonyls.

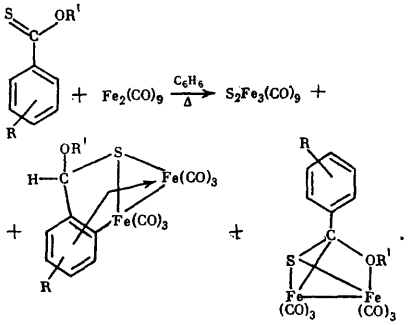
*(d) Reactions of thiobenzophenones with INC.* A cluster of type (II) has been obtained as a side product in 5.4–18.3% yield by the reaction of various thiobenzophenones with $Fe_2(CO)_9$ in benzene at room temperature together with clusters of the type $(C_6H_5)_2CS_2.Fe_2(CO)_6$ (Scheme 3).[56,57] The main compounds were the corresponding *ortho*-metallated complexes formed in most cases in high yields.

Scheme 3



*(e) Reactions of thioesters with INC.* In contrast to the reaction described above, treatment of various *o*-alkyl- and *o*-aryl-thioesters in benzene at room temperature leads mainly to the formation of mixed isomeric diiron hexacarbonyl clusters containing oxygen and sulphur as electron-donating ligands (Scheme 4). Insignificant amounts of the *ortho*-metallated product and a compound of type (II) have been isolated (0.7–7.5%).[51,58,59]

Scheme 4

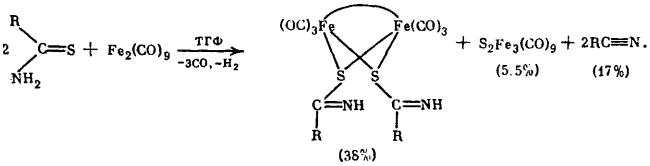


*(f) Reactions of thiourea and thioamides with INC.* Under analogous conditions, substituted thiourea and a series of thioamides react with $Fe_2(CO)_9$ to produce iron tetracarbonyl clusters containing sulphur as the ligand, diiron hexacarbonyl clusters with mixed ligands, and traces (0.1–2.5%) of cluster (II):[17,60–62]

$$RNHCR' + Fe_2(CO)_9 \xrightarrow[\Delta]{C_6H_6} S_2Fe_3(CO)_9 + RNHCR' + [RNHCR']_3 + (RNCR')_2Fe_3(CO)_6.$$

Compound (II) is formed in 5.5% yield on treatment of $Fe_2(CO)_9$ with *p*-methoxythiobenzamide in tetrahydrofuran (THF) at room temperature for 24 h.[17] It is of interest to note that compound (II) is formed via a stage involving the formation of the diiron hexacarbonyl cluster (38%) with subsequent substitution of part of the ligand by the iron tricarbonyl fragment and the isolation of *p*-methoxybenzonitrile (yield 17%, Scheme 5):[60,61]

Scheme 5



*(g) Reactions of thionoadamantanes with INC.* The main product of the interaction of thionoadamantane with $Fe_2(CO)_9$ is the complex $C_{16}H_{14}S_2Fe_2O_6$ (71.5%) which is sensitive to air and differs from the product of the reaction of thiobenzophenone, containing both bridging and terminal carbonyl groups and two sulphur atoms attached to the same carbon atom.

At the same time in the reactions of thiocamphenilone with the complexes mentioned above, compound (II) was isolated as a side product (1.9%), while the reaction of thiofenchone gives rise to a mixture of compounds (I) and (II) (4.6 and 15.7% respectively)[61] [Ref.62? (Ed. of Translation)].

In addition traces of compound (II) have been isolated in the reaction of 2-thiono-1,3-dioxolanchromium pentacarbonyl with $Fe(CO)_5$ on irradiation in THF[63] and on interaction of diphenylthionocyclopropene with $Fe_2(CO)_9$ in THF.[64] Later the formation of ligands of a new type on treatment of diphenylthionocyclopropene with the carbonyl $Fe_2(CO)_9$ and the study of the crystal structures of carbene complexes with a cluster skeleton, namely $Fe_3S_2$, $C_3(C_6H_5)_2Fe_3S_2(CO)_8$, and the dithiodiketone derivative

$C_6(C_6H_5)_4S_2Fe_2(CO)_6$ were described.[65] When the sulphur diimide R–N=S=N–R [R = t-$C_4H_9$ or 4-$(CH_3)C_6H_4$] was treated with $Fe_2(CO)_9$, very small amounts of clusters (I) and (II) were isolated and analysed by a highly sensitive liquid chromatographic technique[66] together with dinuclear and trinuclear iron carbonyl clusters (Scheme 6).[67,68]

*(h) Reactions of carbon disulphide with DDCI.* The compound $S_2Fe_3(CO)_9$ was obtained together with the main product $(CS)SF_4(CO)_{12}$ and two unidentified complexes in the reaction of carbon disulphide with $Fe_3(CO)_{12}$ (in hexane at 80 °C, 10 atm, CO : Ar = 1 : 1, 7.5 h).[69] Only the overall yield of the four compounds is quoted (4%). In addition, the compound $S_2Fe_3(CO)_9$ was isolated in 8% yield together with the octacarbonyl cluster $(C_3H_2S_2)Fe_3(CO)_8S_2$ (43%) as the main product in the reaction of a 1,3-dithiole2-thione with $Fe_2(CO)_9$.[70]

The cluster $S_2Fe_3(CO)_9$ was also obtained as a side product in the reaction of $C_6H_5P(S)Cl_2$ with DDCI in the presence of magnesium in THF together with the mixed-ligand trinuclear cluster $(\mu_3\text{-}S)(\mu_3\text{-}PC_6H_5)Fe_3(CO)_9$ (17%) and the already known $(\mu_3\text{-}PC_6H_5)_2Fe_3(CO)_9$.[71]

The formation of hydrothiocarbonylferrate cluster anions $H_{2-n}Fe_3(CO)_9S^{n-}$ ($n$ = 1,2) has been reported.[72] Such anions, $HFe_3(CO)_9S^-$ or $Fe_3(CO)_9S^{2-}$, are formed when the hydride clusters $HFe_3(CO)_9(SR)$ are heated in polar solvents.[73,74]

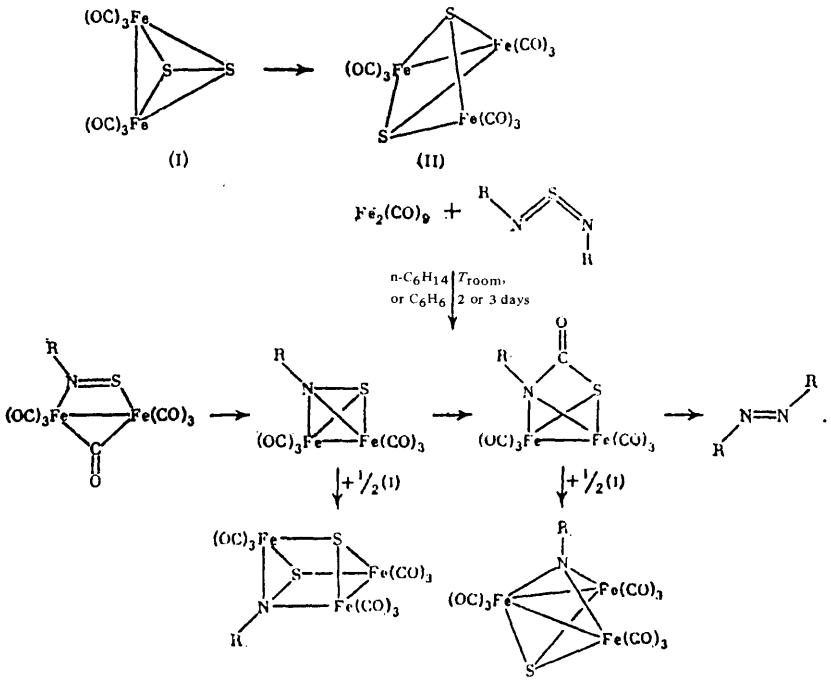
Thus it is seen from the foregoing that the trinuclear cluster $S_2Fe_3(CO)_9$ is a permanent side product in the interaction of iron carbonyls with various organosulphur compounds; it has been shown[3] that, according to TLC data, the initial product is dithiodiiron hexacarbonyl $S_2Fe_2(CO)_6$, which is subsequently converted into a compound of type (II). Methods for the separation of mixtures of compounds (I) and (II) are described in the same communication.[3] It has been found that cluster (II) is fully decomposed and cluster (I) is quantitatively isolated in column chromatography using alumina and n-hexane as the eluent. Refluxing of alcoholic solutions of a mixture of compounds (I) and (II) also decomposes fully compound (II), while cluster (I) is isolated in 72% yield (methanol) and 92% yield (isopropyl alcohol). On the other hand, refluxing of benzene solutions leads to the formation of only the trinuclear cluster (II) in 92% yield. The above results are important not only for the separation of a particular cluster in a pure form but also for the selection of conditions for reactions involving these compounds.

The principal methods of synthesis of the compounds $S_2Fe_2(CO)_9$ and $S_2Fe_3(CO)_9$ are surveyed in the Table. Analysis of the tabulated literature data shows that three methods are the most promising for the synthesis of a mixture of clusters (I) and (II): (1) from elemental sulphur and DDCI (in THF);[3] (2) from hydrogen sulphide and DDCI (in benzene);[4] (3) from elemental sulphur and TSUTH (in benzene).[3] The interaction of $H_2C\text{–}\underset{\underset{S}{\diagup}}{CH}\text{–}CH_2Cl$[5] or $(C_6H_5)_3CSH$[6] with DDCI must be regarded as the most effective method of synthesis of the trinuclear cluster (II).

## III. STRUCTURE AND PHYSICAL RESEARCH METHODS

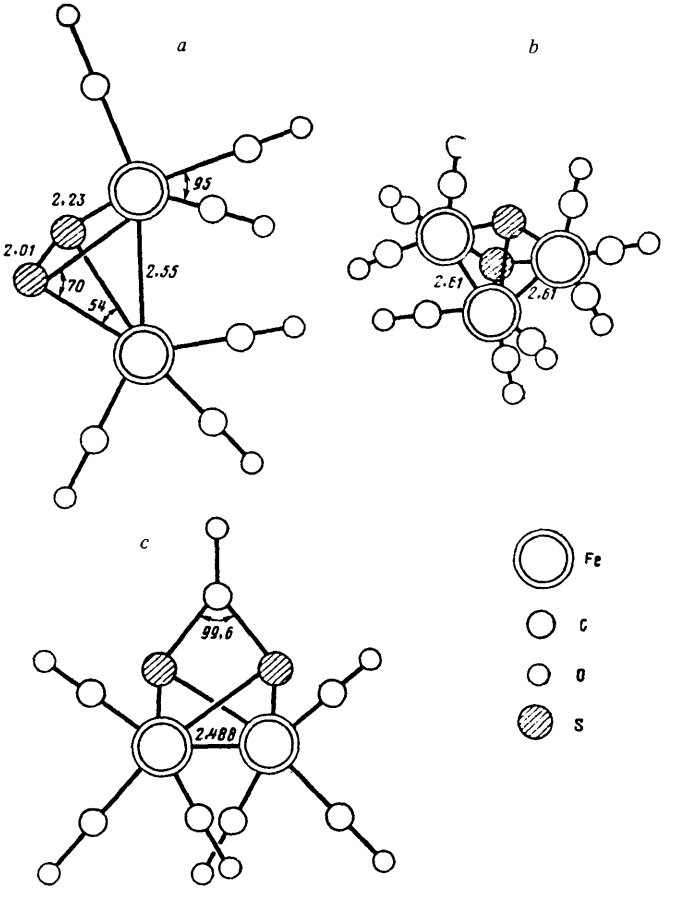
The structures of the compounds $S_2Fe_2(CO)_6$,[75] $S_2Fe_2(CO)_7$,[20] $S_2Fe_3(CO)_9$,[76] $SFe_3(CO)_{10}$,[22] $Se_2Fe_3(CO)_9$,[35] and $Te_2Fe_3(CO)_9$[37] were established by X-ray diffraction. Fig. *a* illustrates the structure of a sulphur-containing cluster of type (I). Evidently the –S–S– ligand is a bridge linking symmetrically two iron atoms; the iron–iron distance corresponds

Scheme 6



to the formation of a metal–metal bond. Fig.*b* shows that the sulphur-containing cluster of type (II) contains a triangle of iron atoms: the lengths of the two Fe–Fe bonds are on average 2.6 Å, while the third side of the triangle is 3.37 Å long. Subsequently it was established that, on passing to the analogous clusters containing selenium[35] and tellurium,[37] all the metal–metal bonds become so much longer that in the structure of the $Te_2Fe_3(CO)_9$ cluster the three $Fe(CO)_3$ fragments are in essence linked to one another only via $\mu_3$-tellurium bridges.

It has been shown by X-ray diffraction that the structure of the cluster $[\mu\text{-S–C(O)–S–}]Fe_2(CO)_6$ corresponds to the insertion of CO in the S–S bond (Fig.*c*).[20] It has also been demonstrated with the aid of the same method that the $\mu_3$-bridging sulphide and CO ligands in the cluster $(\mu_3\text{-S})(\mu_3\text{-CO})Fe_3(CO)_9$ "build-up" the triangle of Fe atoms to a trigonal bipyramid (the number of valence electrons associated with the three Fe atoms is 48).[22]




The structures of the $(\mu\text{-S})_2Fe_2(CO)_6$ (*a*), $(\mu_3\text{-S})_2Fe_3(CO)_9$ (*b*), and $[\mu\text{-S–C(O)–S–}]Fe_2(CO)_6$ (*c*) clusters.

The relation between the number of atoms, the number of bonding electron pairs (skeletal electrons) and the geometrical structure of cluster compounds has been examined[77,78] and the different types of geometrical structures of cluster compounds have been classified as a function of the number of atoms in the cluster, and simple rules have been formulated for the calculation of the number of bonding electron pairs in cluster compounds of different types. Such calculation makes it possible to explain the known structures and to predict the unknown structures of the known compounds as well as the existence of new compounds and methods for their synthesis. In particular, certain possible transformations of geometrical structures of one type into those of another type in reactions accompanied by a change in the number of skeletal electrons of a given cluster have been examined and the interaction of compound (II) with $L_3M(CO)_3$ has been described, but has not so far been confirmed experimentally:

$$S_2Fe_3(CO)_9 + L_3M(CO)_3 \rightarrow (OC)_3MS_2Fe_3(CO)_9 + 3L;$$
$$L = CO, RCN;\ M = Cr, Mo, W.$$

The results of quantum-chemical calculations by the self-consistent field method (SCF–$X_\alpha$–SW) have been compared[79,80] with data obtained from the photoelectron spectra of the $S_2Fe_2(CO)_6$ molecule and it has been established that the Fe–Fe bond is best described in terms of a simple "bent" bond, while the orbital corresponding to it has the character of the highest occupied molecular orbital (HOMO).

The infrared and Raman spectra of $S_2Fe_2(CO)_6$ and the $(CH_3S)_2Fe_2(CO)_6$ isomers have shown[81] that the Fe–Fe bond stretching vibrations are at 191 $cm^{-1}$; the force constant of this bond is 1.3 mdyn $A^{-1}$ and is close to the value expected for a single Fe–Fe bond. Study of the infrared spectra in the CO group stretching region, in hexane solutions of a series of dinuclear bridged carbonyl complexes of the type $Y_2Co_2(CO)_6$, where Y = CO, P, As, or CR, and $X_2Fe_2(CO)_6$, where X = S, SR, Se, PRR′, Br, or I, both with normal and enriched in $^{13}CO$, established that the difference between the force constants for the axial and equatorial CO groups (the latter are in the *trans*-position relative to the bridging ligand) characterises the $\pi$ interaction of the metal with the bridging group.[82]

The dimeric character of the clusters $[XFe(CO)_3]_2$, where X = S, Se, $SC_2H_5$, $SeC_2H_5$, or $SC_6H_5$, has been demonstrated by their diamagnetism and also by the results of cryoscopic studies of these compounds (in benzene). The dipole moments of type (I) clusters considered, with X = S, Se, or $SC_2H_5$, in benzene and of a compound of type (I), with X = $SC_2H_5$, dissolved in cyclohexane are respectively 1.63 ± 0.1, 2.20 ± 0.07, 2.69 ± 0.05, and 2.66 ± 0.04 D,[83] which also indicates their dimeric character. The authors proposed for them non-planar bridged structures analogous to those which were later established by X-ray diffraction (Fig.*a*).

The $^{13}C$ NMR spectra have been investigated in a series of studies[84–87](including the observation of satellites due to the $^{57}Fe$ nucleus) for a series of clusters: $S_2Fe_2(CO)_6$ and the *syn*- and *anti*-isomers of $(CH_3S)_2Fe_2(CO)_6$ and $Fe_3(CO)_{12}$. The information obtained indicates the retention in solution of the structures established for these compounds in the crystal state. On varying the experimental temperature, intramolecular dynamic processes were discovered but their nature has not been accurately established.

The electronic structure of the dinuclear clusters (I) and their analogues containing metal–metal bonds has been studied[88] with the aid of He(I) and He(II) photoelectron spectra.

The Mössbauer spectra of the compounds $S_2Fe_3(CO)_9$, $Se_2Fe_3(CO)_9$, and $R_3PS_2Fe_3(CO)_8$ have been investigated by $\gamma$-nuclear resonance.[89–92] The mass spectra of $X_2Fe_2(CO)_6$ (X = S or Se) and $X_2Fe_3(CO)_9$ (X = S, Se, or Te) have been

published.[93] The data obtained have been compared with the results of thermogravimetric analysis of thermal decarbonylation, of the same clusters in the temperature range 25–600 °C. After decarbonylation, the residues were subjected to X-ray diffraction and magnetic investigations.[93]

The mass spectrum of compound (II) contains the molecular ion as well as ions formed as a result of the successive elimination of the nine CO groups. The maximum peak is that of the $S_2Fe_3^+$ ion, which subsequently decomposes with formation of $S_2Fe_2^+$ and $Fe_2^+$.[94] Mass spectrometric studies on the negative ions formed from $X_2Fe_3(CO)_9$ (X = S, Se, or Te) have been reported.[95] The peak of the $X_2Fe_3(CO)_7^-$ ion proved to be the most intense and a weak molecular peak due to $Te_2Fe_3(CO)_8^-$ was also observed.

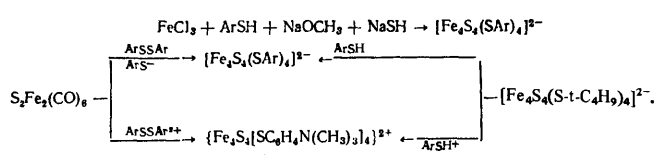
Study of the oxidation-reduction reactions of the cluster $Cp_3Fe_3(CO)_2(S)(SR)$ by the cyclic voltamperometric method revealed the presence of two waves on the voltage–current plots corresponding to two reversible oxidation-reduction processes.[96,97] The voltage–current plot for $S_2Fe_3(CO)_9$ showed only one wave, whose potential was more negative than for $Cp_3Fe_3(CO)_2(S)(SR)$. The smaller chemical shift in the $^{57}Fe$ Mössbauer spectra of the cluster $Cp_3Fe_3(CO)_2(S)(SR)$ compared with $S_2Fe_3(CO)_9$ shows that the CO groups in the former cluster are more powerful π-acceptor ligands than the terminal CO groups in the latter cluster.[97]

## IV. CHEMICAL PROPERTIES

The advance achieved nowadays in the chemistry and physics of cluster compounds have brought to the fore the task of investigating their reactivities and their unique properties, which in many respects have altered traditional ideas about the reactivity of coordination and organometallic compounds.

### 1. The Conversion of Type (I) Clusters into Cubane Clusters

Considerable advances have been made in the synthesis and study of clusters having the general formula $[Fe_4S_4(SR)_4]^{n-}$, where R is an alkyl or aryl group. The structures of these synthetic analogues of proteins, established by X-ray diffraction, and their spectroscopic and magnetic properties are very similar to those of clusters found in the so-called "proteins with a high potential" (PHP) and in oxidised ferredoxin.[98] The synthesis of cubane clusters of the $Fe_4S_4$ type from a carbonyl-containing compound of type (I) has been described.[99] The preparation of the corresponding cluster and the specific syntheses from known compounds proceed in accordance with the following scheme:




The reaction mixture containing $S_2Fe_2(CO)_6$, $C_6H_5SSC_6H_5$, and $C_6H_5S^-$ in molar proportions of 1 : 1 : 2 yields $[Fe_4S_4(SC_6H_5)_4]^{2-}$ as the only product, which was isolated and identified in the form of the tetraphenylarsonium salt (65% yield):

$$S_2Fe_2(CO)_6 + C_6H_5SSC_6H_5 + C_6H_5SH + (C_6H_5)_4AsCl \xrightarrow[1\ h,\ CH_3OH,\ \Delta]{CH_3ONa,\ N_2} [(C_6H_5)_4As]_2\{Fe_4S_4(SC_6H_5)_4\} + CO + NaCl.$$

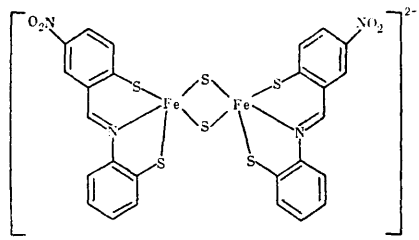
The cationic tetramer was obtained in the following way:

$$S_2Fe_2(CO)_6 + (n\text{-}(CH_3)_3NC_6H_4S)_2(PF_6)_2 + [n\text{-}(CH_3)_3NC_6H_4SH]PF_6^+ + CH_3ONa \xrightarrow[N_2,\ 1\ h,\ \Delta]{CH_3OH\text{–}CH_3CN} \{Fe_4S_4[SC_6H_4N(CH_3)_3\text{-}n]_4\}^{3+} + CO + NaPF_6.$$

According to the authors,[99] the carbonyl groups in compound (I) are initially fully substituted by the thiyl fragment with formation of the $Fe_2S_2$ cluster, which is followed by thermal or catalytic dimerisation:

$$S_2Fe_2(CO)_6 + RSSR + 2RS^- \rightarrow [S_2Fe_2(SR)_4]^{2-} + 6CO;$$
$$2[S_2Fe_2(SR)_4]^{2-} \rightarrow [S_3Fe_4(SR)_4]^{2-} + RSSR + 2RS^-.$$

The interaction of 2,2-bis{benzo[*d*]thiazoline}-4,4-dinitrodiphenyl disulphide with compound (I) in the presence of sodium methoxide was investigated in the same study.[99] The corresponding anionic cluster, free from carbonyl groups, was identified in the form of the tetraphenylarsonium salt. The authors suggest that the cluster contains pentacoordinate iron(III). An analogous cluster has been obtained by the reaction of $FeCl_3$, NaSH, and a base with thiazoline disulphide.




### 2. Reduction Reactions of Type (I) Clusters

Treatment with reducing agents such as KH, metallic sodium, and the RLi–LiBr (R = $CH_3$ or $C_4H_9$) system leads to the cleavage of the S–S bond in compound (I).[100,101] The authors suggest the initial formation of both the monoanion (A) and the corresponding dianion (B), which subsequently readily enters into condensation reactions, for example, in accordance with the following scheme:

$$S_2Fe_2(CO)_6 + CH_3Li/LiBr \xrightarrow[-78^\circ]{(C_2H_5)_2O,\ N_2} \underset{(A)}{[(CH_3S)_2Fe_2(CO)_6]^-} \xrightarrow[12\ h]{CH_3I} \underset{(82\%)}{(CH_3S)_2Fe_2(CO)_6};$$
$$S_2Fe_2(CO)_6 + KH \xrightarrow[4\ h]{THF,\ N_2} \underset{(B)}{[S_2Fe_2(CO)_6]^{2-}} \xrightarrow{CH_3I} \underset{(53\%)}{(CH_3S)_2Fe_2(CO)_6}.$$

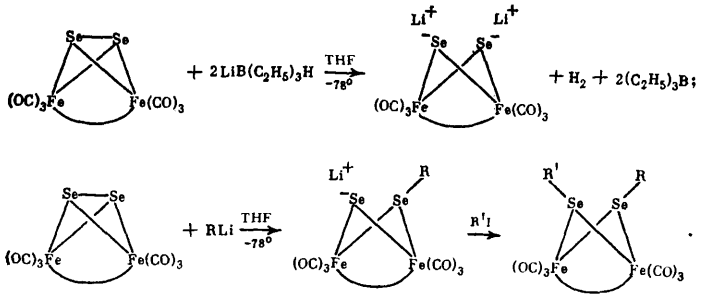
This leads to a way of synthesising various asymmetric bis(alkylthio)diiron hexacarbonyl clusters from the monoanion (A). The dianion (B) is of considerable interest for the synthesis of already known iron sulphide clusters containing both acyclic and cyclic groups.[101] An improved method of synthesis of the dianion (B) for compound (I) into THF by treatment with $LiB(C_2H_5)_3H$ has been proposed.[102]

The reactions of the dianion (B) with organic halides and with tin, germanium, silicon, and nickel halides have also been reported.[102] The protonation of the dianion (B) by treatment with $CF_3COOH$ leads to the formation of the bridged thiol cluster $(HS)_2Fe_2(CO)_6$ in a quantitative yield. Its synthesis and some of its properties have been described in detail in two communications.[103,104] This thiol cluster has been used to synthesise the $S_2Fe_2(CO)_6$ clusters in the study of the chemistry of these compounds.[105]

It has been found[34] that the reactivity of diselenodiiron carbonyl $Se_2Fe_2(CO)_8$ (VI) is the same as that of the usual organic diselenides RSeSeR. Thus the reaction with two molar equivalents of $LiB(C_2H_5)_3H$ converts compound (VI) into the dianion $(LiSe)_2Fe_2(CO)_6^{2-}$. Organolithium reagents

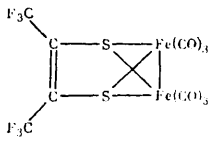
cleave the Se–Se bond in compound (VI), affording (μ-LiSe).(μ-RSe)$Fe_2(CO)_6$ [34] by analogy with the sulphur-containing cluster (Scheme 7).[101]

Scheme 7



### 3. Interaction of Compounds of Type (I) with Activated Acetylenes

The photochemical effect of activated acetylenes (hexafluorobut-2-yne or dimethyl or diethyl acetylenedicarboxylate) on dithiodiiron hexacarbonyl $S_2Fe_2(CO)_6$ in THF leads to their insertion in the cluster not in the Fe–Fe bond, as happens for $(RS)_2Fe_2(CO)_6$,[106] but in the S–S bond[107] with formation of a dithiolene cluster of the type



whose structure has been demonstrated by specific synthesis.[107]

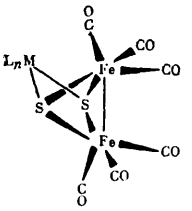
### 4. Reactions Involving Addition to Type (I) Clusters

It has been shown recently[108] that lithium alkyls also add to $S_2Fe_2(CO)_6$ at the S–S bond.

An unexpected intramolecular nucleophilic substitution in the anionic complex of $Fe_2(CO)_6$ with an organosulphur ligand has been observed.[109] It can be regarded as a new method of synthesis of complexes of $Fe_2(CO)_6$ with dithioformic acid esters. Later the same workers[110] discovered the formation of an exocluster sulphonium group from the product of the deprotonation of the diiron hexacarbonyl complex of thioformic acid ester.[111]

### 5. Reactions of Type (I) Compounds with Metal Complexes

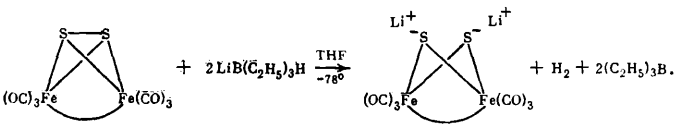
The reactions of dithiodiiron hexacarbonyl can only involve the S–S bond, which constitutes a feature of this compound similar to that of organic disulphides. The reaction of compounds (I) with metal complexes in the zerovalent state, such as $[(C_6H_5)_3P]_4Pt$, $[(C_6H_5)_3P]_3Pd(CO)$, and $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Ni(CO)_2$ entails the insertion of Ni, Pt, and Pd in the S–S bond, and under mild conditions (benzene, 20 °C, 2.5–24 h) the products are the coloured crystalline complexes $QM(S)_2Fe_2(CO)_6$ where Q = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ or $[(PC_6H_5)_3]_2$ and M = Ni, Pd, or Pt, which are stable in air.[112]



Analogous products have been obtained by the reaction of the dianion (B) with the corresponding metal chlorides.[112]

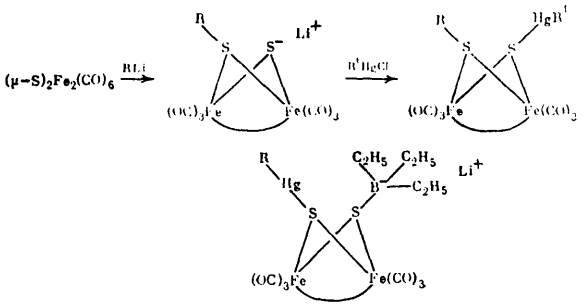
The transfer of the alkyl group from the boron atom to the sulphur atom in the reactions of lithium hydrotriethylborate derivatives of the bis(μ-thiolato)-bis(tricarbonylferrate) dianion with mercury and alkylmercury chlorides has been described.[113] The reactions of $(\mu\text{-LiS})_2Fe(CO)_6$, obtained by the interaction of $S_2Fe_2(CO)_6$ and $LiB(C_2H_5)_3H$ with $HgCl_2$ in THF in accordance with Scheme 8, in methyl, ethyl, or propyl alcohol, or in THF give rise to the product of the previously unknown transfer of the alkyl group from the boron atom to the sulphur atom: $(\mu\text{-SC}_2H_5)$. $(\mu\text{-SHgC}_2H_5)Fe_2(CO)_6$.

Scheme 8



The formation of elemental mercury in this reaction led the authors[112] to the hypothesis that RHgCl acts as an oxidant, oxidising the intermediate complex [shown in Scheme 9] and leading to the transfer of the ethyl group from boron to sulphur, yielding ultimately the observed product, for which four isomers are possible according to $^1H$ and $^{13}C$ NMR spectra (Scheme 9).[113]

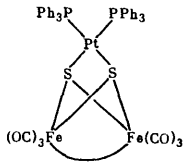
Scheme 9



An interesting comparison of the reactivities of the carbonyl dianion $[S_2Fe_2(CO)_6]^{2-}$ and the anion of Roussin's red salt $[S_2Fe_2(NO)_4]^{2-}$ has been made in a report,[114] which describes also certain chemical properties of Roussin's red salt, in particular its reactions with monofunctional electrophiles RX[R = $CH_3$, $C_2H_5$, $CH_2=CHCH_2$, $C_6H_5CH_2$, $CH_3Sn$, $(C_6H_5)_3Sn$, $(C_6H_5)_3Pb$, $C_6H_5Hg$, or $CpFe(CO)_2$; X = halogen], resulting in the formation of the related nitrosyl complexes $(RS)_2Fe_2(NO)_4$ and NaX.

The synthesis and the structure of the bridged platinum derivative of Roussin's red salt (Scheme 10) are described in the subsequent communication by the same authors.[115]

Scheme 10



$$+ 4NO \longrightarrow (Ph_2P)_2PtS_2Fe_2(NO)_4 + 6CO.$$

The same derivative has been synthesised by the reaction of $Na_2[Fe_2(S)_2(NO)_4]$ with *cis*-$[(C_6H_5)_3P]PtCl_2$ in THF.[115]

## 6. The Insertion of Group IVB Elements in Type (I) Clusters

Group IVB elements can be inserted into a cluster (I) both in the S–S and Fe–Fe bonds. The compounds formed may be of definite interest, because fragments capable of entering into numerous reactions remain in both cases.

It has been shown[116] that the reaction of compound (I) with the triethylamine complex of trichlorosilane (pentane, 1 h, 40 °C) results in the formation of bis(hexacarbonyldithiodiiron)silicon (73%):

$$S_2Fe_2(CO)_6 + HSiCl_3\cdot(C_2H_5)_3N \rightarrow Si[S_2Fe_2(CO)_6]_2.$$

When methanolic solutions of compound (I) and the triethylamine complex of trichlorogermane are mixed, a brown-red precipitate of bis(dithiodiiron)germanium is formed instantly at room temperature (82%):[116,117]

$$S_2Fe_2(CO)_6 + HGeCl_3\cdot(C_2H_5)_3N \rightarrow Ge[S_2Fe_2(CO)_6]_2.$$

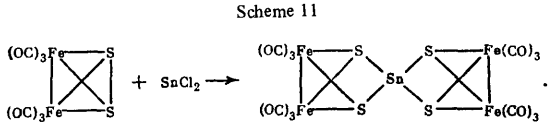
The structure of this cluster has been established.[118]

The reaction involving the dissociation of the S–S bond in compound (I) after preliminary treatment with various reducing agents (with formation of the corresponding dianions) has also been achieved and a complex containing the $(CH_3)_2Sn$ fragment has been obtained.[101] In contrast to the triethylammonium salts of trihalogenogermanes(silanes), the corresponding $HSnCl_3$ salt does not react with dithiodiiron hexacarbonyl.[3] At the same time refluxing of a solution of a type (I) cluster in absolute ethanol with the tribromostannane–amine complex leads to the formation of a product containing two molecules of the amine complex and one molecule cluster (I) (according to the results of elemental analysis and the infrared spectra):

$$S_2Fe_2(CO)_6 + (C_2H_5)_3N\cdot HSnBr_3 \rightarrow S_2Fe_2(CO)_6\cdot 2(C_2H_5)_3N\cdot HSnBr_3.$$

Treatment of compound (I) with tin dichloride in solution in methanol, ethanol, and a methanol–ethyl acetate mixture (4 h, 65 °C) gives rise to a compound in which the $SnCl_2$ : (I) ratio is 1 : 2 (on the basis of the results of elemental analysis) (Scheme 11).[3]

Scheme 11



## 7. Reactions of Compound (I) with Diazomethane

When compound (I) was allowed to react with diazomethane in ether at temperatures ranging from −40° to 20 °C, a brown deposit consisting of fractions having different molecular weights was obtained.[119] Treatment of the deposit with pentane and subsequent chromatography on $Al_2O_3$ or silica gel led to the isolation of various methylene-, bismethylene-, methyl-, and trismethylene-dithiodiiron hexacarbonyl clusters with the main high-molecular-weight $[H_2C = S_2Fe_2(CO)_6]_x$ fraction, which is insoluble in the usual organic solvents.[119]

## 8. The Effect of Halogens on Compounds (I) and (II)

The first data concerning the effects of the halogens on sulphur cluster complexes have been published by Hieber and Kaiser.[120] The reactions of dinuclear carbonyliron mercaptides $(C_2H_5S)_2Fe_2(CO)_6$ with halogens leads to compounds of the type $[C_2H_5SFe(CO)_3X]_2$ (X = Br or I). The phosphine-substituted compounds $[Fe(CO)_2LX]_2$ [L = $P(C_6H_5)_3$; X = S, $SC_2H_5$, or $SC_6H_5$] react with iodine to form the periodides $[Fe(CO)_2LXI_{0.5}]^+_2I_3$, while salts of a trinuclear cation of the type $[Fe_3(CO)_4L_2X_2Hal_4]^+Hal^-$ are formed when the unsubstituted compounds $[Fe(CO)_3LX]_2$ react with chlorine, bromine, or iodine (Hal). Compounds of the last two types are isolated from aqueous mediums as salts, for example, $[Fe(CO)_2LXHal_{0.5}]^+_2[PF_6]^-$.[120]

The reactions of the trinuclear dithiotriiron carbonyl of type (II) with the halogens lead to the formation of a trinuclear cluster cation under the same conditions: $[Fe_3(CO)_6\cdot S_2Hal_4]^+Hal^-$.[120]

## 9. Reactions Involving the Substitution of Ligands in Compounds (I)

We shall consider initially the reactions leading to the cleavage of the S–S bond in compounds (I) and in the same reactions involving compounds (II).

For the carbonylthio-clusters considered, there exist two examples of the complete substitution of carbonyl groups. The first concerns the preparation of synthetic analogues of iron- and sulphur-containing proteins (ferredoxins)[99] and the second the reaction of compounds (II) with bis(trifluoromethyl)dithioethane.[121]

The reaction of compound (II) with $S_2C_2(CF_3)_2$ affords a high yield of $S_2Fe_3[S_2C_2(CF_3)_2]_4$,[121] which has also been synthesised from $(CF_3)_2C_2S_2Fe_2(CO)_6$ and sulphur.[122] This is a novel method of synthesis of trinuclear clusters not containing carbonyl fragments.

Certain carbonyl groups in metal carbonyls are known to be readily substituted by phosphines, arsines, and stibines, but for the majority of metal carbonyls the removal of all the carbonyl groups presents considerable difficulties; this can be achieved only in reactions with triphenylphosphine.[7,45,123,126]

The interaction of the sulphur-containing cluster (I) with triphenylphosphine at room temperature has been described. It leads to the formation of a disubstituted cluster whose molecular weight has been determined:[127]

$$S_2Fe_2(CO)_6 + 2P(C_6H_5)_3 \xrightarrow[20°]{C_7H_{16}} [(H_5C_6)_3P]_2S_2Fe_2(CO)_4] + 2CO.$$

The reactions of $X_2Fe_2(CO)_6$, where X = S or Se, with a ligand L lead to various products, whose formation depends on the nature of both L and X.

When the less reactive $Se_2Fe_2(CO)_6$ is treated with $As(C_6H_5)_3$ or $P(OC_6H_5)_3$, mainly the monosubstituted product (A) and to a lesser extent the disubstituted compound (B) are formed; polynuclear complexes were not detected.[127]

$$Se_2Fe_2(CO)_6 + L \rightarrow \underset{(A)}{LSe_2Fe_2(CO)_5} + CO;$$

$$LSe_2Fe_2(CO)_5 + L \rightarrow \underset{(B)}{L_2Se_2Fe_2(CO)_4} + CO;$$

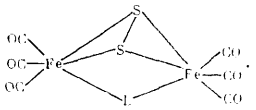
$$L = As(C_6H_5)_3,\ P(OC_6H_5)_3.$$

It is important to note that the interaction of compound (I) with $P(C_6H_5)_3$ leads initially to the formation of the compound $(C_6H_5)_3PS_2Fe_2(CO)_6$, which, however, has not been isolated.[127] It has been characterised only by infrared spectroscopy, together with $(C_6H_5)_3PS_2Fe_2(CO)_5$. The difficulty of isolating this cluster is probably associated with its instability and high reactivity. The main reaction products are the corresponding mono- and di-substituted derivatives (I) and (II).

The same workers[127] have shown that, when $P(OC_6H_5)_3$ is used, the unstable compound $(C_6H_5O)_3PS_2Fe_2(CO)_5$ is formed as an intermediate. The reaction mixture also contains mono- and di-substituted derivatives of compounds (I) and (II). It has been suggested that the trinuclear clusters are formed via a stage in which an intermediate complex is produced on interaction of compound (I) with the mono-derivative or the adduct.[127]

The greater difference between the reactivities of $As(C_6H_5)_3$ and $P(n\text{-}C_4H_9)_3$ in their reactions with compound (I) shows that the preliminary dissociation of the initial complex is unlikely and that the ligand is coordinated to compound (I) with formation of an adduct:

$$S_2Fe_2(CO)_6 + L \rightarrow LS_2Fe_2(CO)_6;$$
$$L = P(C_6H_5)_3,\ P(n\text{-}C_4H_9)_3;$$



A structure in which the ligand is formally coordinated to two iron atoms, forming a labile three-centre donor–acceptor bond, has been proposed for the adduct.

The dinuclear chalcogeniron carbonyl clusters $L_2(CH_3S)_2 \cdot Fe_2(CO)_4$, formed in the reactions of compounds (I) with a proton[128] and $HgCl_2$,[129] as well as the salt-like complexes with the halogens, namely $[Fe(CO)LL'(SR)]_2$ (L' = CO, phosphine, or phosphite), frequently have a similar structure.[130] An additional piece of evidence for the formation of adducts in the above systems is, according to the authors,[131] the oxidative addition of $(CF_3)_2C_2S_2$ or $NOPF_6$ to compounds (I), leading to the formation of the cationic complex $[Fe_2(SR)_3(CO)_6]^+$, in which the SR group is inserted in the Fe–Fe bond. The structure of this compound has been established by X-ray diffraction.[132]

Monosubstituted derivatives of compound (I) are readily generated from the adduct as a result of the migration of the ligand to one of the iron atoms with the simultaneous elimination of a CO group in accordance with the equation

$$LX_2Fe_2(CO)_6 \rightarrow LX_2Fe_2(CO)_5 + CO.$$

The subsequent attack by the iron atom on a second molecule of L leads to the formation of a disubstituted derivative of compound (I).[130]

The stability of the substitution products depends on the nature of the ligand,[45] apparently owing to the formation, on successive substitution, of a system having an exess electron density of the iron atoms, which promotes the mutual repulsion of the latter. An analogous influence of the nature of the cations on the stability of compounds with an Fe–Fe bond has been demonstrated in another study.[133]

The kinetics of CO substitution in $X_2Fe_2(CO)_6$ clusters (where X = S or Se) by ligands such as $As(C_6H_5)_3$, $P(OC_2H_5)_3$, $P(OC_6H_5)_3$, or $P(C_6H_5)_3$ has been investigated by infrared and ultraviolet spectroscopy.[134] A possible mechanism of the reactions of compounds (I) with L has been proposed, according to which the rate-determining reaction stage involves the formation of the associated species $X_2Fe_2(CO)_6L$, which subsequently loses a CO group with formation of a monosubstituted product or again reacts with a molecule of compound (I), giving rise to a trinuclear derivative via an intermediate of the type $X_2Fe_2(CO)_6L\ldots X_2Fe_2(CO)_6$:

$$X_2Fe_2(CO)_6 \underset{-L}{\overset{+L}{\rightleftarrows}} X_2Fe_2(CO)_6L \begin{cases} \xrightarrow{+L} \text{products;} \\ \xrightarrow{-CO} X_2Fe_2(CO)_5L \xrightarrow{+L} X_2Fe_2(CO)_4L_2; \\ \xrightarrow{+X_2Fe_2CO_6} [X_2Fe_2(CO)_6L\ldots X_2Fe_2(CO)_6] \rightarrow X_2Fe_3\text{-derivatives.} \end{cases}$$

The proposed structure of the "secondary" adduct is extremely doubtful, although it does not conflict with the possibility of the coordination of compound (I) to the initial adduct at the S–S bond.[134]

The adduct can react via different mechanisms, serving as the starting compound for the preparation of polynuclear clusters. It has been noted[134] that the yield of these clusters is a maximum when the concentrations of compound (I) and of L are a maximum.

The rate constants for the above reactions indicate the high sensitivity of compound (I) to the nature of the attacking ligand L, which can be explained, according to the authors,[134] by the ease of their coordination to the Fe atom.

## 10. Ligand Substitution Reactions Involving Compounds (II)

Numerous studies involving the substitution of the CO groups in the compounds $X_2Fe_3(CO)_9$ (X = S, Se, or Te) with phosphines, phosphites, and arsines have been carried out[126,135–140] and it has been shown[135] that, for X = S or Se, a mixture of mono- and di-substituted derivatives of compound (II) is formed:

$$X_2Fe_3(CO)_9 + L \rightarrow LX_2Fe_3(CO)_8 + CO;$$
$$LX_2Fe_3(CO)_8 + L \rightarrow L_2X_2Fe_3(CO)_7 + CO;$$
$$L = As(C_6H_5)_3,\ P(OC_6H_5)_3,\ P(n\text{-}C_4H_9)_3.$$

$Te_2Fe_3(CO)_9$, behaves differently in the reactions considered. It is characterised by the formation in the first stage of the corresponding adduct with subsequent elimination of a CO group:[135]

$$Te_2Fe_3(CO)_9 + L \rightarrow LTe_2Fe_3(CO)_9;$$
$$LTe_2Fe_3(CO)_9 \rightarrow LTe_2Fe_3(CO)_8 + CO.$$

The synthesis and properties of heterometallic cluster compounds obtained from $Te_2Fe_3(CO)_9$ have been described recently.[141]

The reactivity of the mixed cluster $XYFe_3(CO)_9$ (X and Y = S, Se, or Te; $X \neq Y$) in the reaction involving the displacement of a CO group by a triphenylarsine and triphenylphosphine corresponds to the reactivity of $X_2Fe_3(CO)_9$.[138]

The complexes $LXYFe_3(CO)_8$ and $L_2XYFe_3(CO)_7$ have more than one isomer. The ligand L in the monosubstituted complexes is probably coordinated to the Fe atom adjoining the chalcogen atoms, while in the disubstituted complexes two L molecules are coordinated to two iron atoms owing to steric hindrance. However, it cannot be ruled out that the existence of two and more isomers is a result of the ligand exchange between the iron atoms in the cluster.[138]

The synthesis of derivatives of compound (II) by the substitution of one, two, or three CO groups by triphenylphosphine and nitrogen-containing ligands (phenanthroline, $\alpha,\alpha'$-bipyridyl, acetonitrile, triethylamine, pyridine, and piperidine) has been described.[140] The character of the

infrared spectra of the compounds obtained in the carbonyl region depends on the strength of the $d_\pi$ bonds between the ligand and the metal.

### 11. The Reactions of Compounds (I) and (II) with Transition Metal Carbonyls

The rapid rearrangements of the adduct $X_2Fe_2(CO)_6 \cdot L \ldots X_2Fe_2(CO)_6$ lead to the formation of $X_2Fe_3(CO)_9$ or $LX_2Fe_3(CO)_8$ with loss of L or CO respectively. In this case the adduct behaves as a ligand containing a sulphur atom as the nucleophilic fragment. A similar behaviour of the $AsCo_3(CO)_9$ [84] and $SFeCo_2(CO)_9$ [142,143] clusters, in which the As and S atoms manifest the character of Lewis bases in reactions with $Fe(CO)_5$ and $M(CO)_6$ (M = Cr, Mo, or W), has been reported:

$$SFeCo_2(CO)_9 + M(CO)_6 \rightarrow (OC)_5MSFeCo_2(CO)_9 + CO;$$
$$SFeCo_2(CO)_9 + Fe(CO)_5 \rightarrow (OC)_4FeSFeCo_2(CO)_9 + CO;$$
$$AsCo_3(CO)_9 + M(CO)_6 \rightarrow (OC)_5MAsCo_3(CO)_9 + CO.$$

In the adduct the ligand weakens the S–S bond by increasing the electron density in the $X_2Fe_2$ fragment. Steric and electronic factors influence the electron-donating character of the adduct. For example, tributyl phosphite, which is a powerful ligand donor, ensures a high yield of the trinuclear cluster. The above mechanism makes it possible to interpret the difference between the reactions involving the direct substitution of the CO groups in compound (II) and the formation of $LX_2Fe_3(CO)_8$ from the adduct. On the basis of $^{13}C$ NMR spectra, the authors[143] concluded that the substituted trinuclear clusters synthesised by the two different methods are identical.

It has been shown[144] that heating of a mixture of $(PHR)_2 \cdot Fe_2(CO)_6$ with $Fe_3(CO)_{12}$ leads to the formation of $(PR)_2 \cdot Fe_3(CO)_9$ together with the clusters $(PR)_2Fe_4(CO)_{11}$ and $(PR)_2Fe_4(CO)_{12}$.

The structure of the cluster $(\mu_3\text{-}S)(\mu_3\text{-}PR)Fe_3(CO)_9$ (where $R = p\text{-}CH_3OC_6H_4$), obtained by the reaction of $Fe_3(CO)_{12}$ with the Lawesson reagent cyclo-$[p\text{-}CH_3OC_6H_4P(S)S]_2$, has been determined recently.[145,146]

Treatment of compound (I) with $Fe_3(CO)_{12}$ or $(C_2H_5)_3N \cdot H_2Fe_3(CO)_{11}$ leads to the formation of a compound of type (II):[3]

$$S_2Fe_2(CO)_6 + Fe_3(CO)_{12} \rightarrow S_2Fe_3(CO)_9 + CO.$$

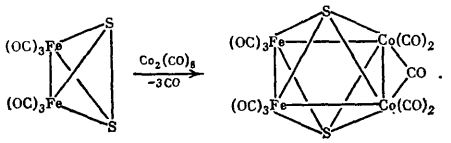
The presence of insignificant amounts of dithiodiiron heptacarbonyl $S_2Fe_2(CO)_7$ in the reaction mixture and the instability of this cluster, which is quantitatively converted into compound (I) in solution, suggests that the above dinuclear cluster can be an intermediate in the formation of the trinuclear cluster (II).[3] The reaction apparently proceeds via a stage involving the formation of compound (I) with subsequent insertion of the $Fe(CO)_3$ fragment in the S–S bond.

Dicobalt octacarbonyl does not react with compound (II), while the sulphur-containing cluster (I) reacts under mild conditions to give a relatively high yield (56%) of $SFeCo_2(CO)_9$,[147] whose structure has been established by X-ray diffraction:[148]

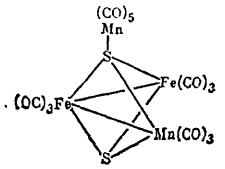
$$S_2Fe_2(CO)_6 + Co_2(CO)_8 \xrightarrow[\Delta]{C_6H_{14},N_2} SFeCo_2(CO)_9 + Fe(CO)_5 + S.$$

Vahrenkamp and Wucherer[149] were the first to synthesise a tetranuclear cluster from two initial dinuclear complexes of type (I). As expected, the substitution by cobalt carbonyl under mild conditions leads to the formation of the new tetranuclear cluster $S_2Fe_2Co_2(CO)_{11}$ (Scheme 12).

Scheme 12



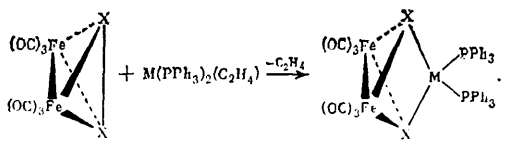

The photoinduced reaction of $S_2Fe_2(CO)_6$ with $Mn_2(CO)_{10}$ in solution in THF gives rise to a cluster having the composition $S_2Fe_2Mn_2(CO)_{14}$.[150] The composition and structure of this cluster, established by elemental analysis, mass spectrometry, Mössbauer spectroscopy, and X-ray diffraction, can be represented by $Fe_2Mn(CO)_9 \cdot (\mu_3\text{-}S)(\mu_4\text{-}S)Mn(CO)_5$, where the $Fe_2Mn$ system contains one Fe–Fe bond and one Fe–Mn bond.[150]




### 12. Oxidative Addition of Metal Complexes

New heterometallic chalcogenide clusters $X_2Fe_2(CO)_6M(PPh_3)_2$ (where X = S, Se, or Te; M = Pt or Pd), characterised by means of elemental analysis, molecular weight measurements, and infrared and NMR spectroscopic data (Scheme 13), have been obtained in quantitative yields by the oxidative addition of $M(PPh_3)_2(C_2H_4)$ to $X_2Fe_2(CO)_6$:[151]

Scheme 13




This reaction has been used to obtain heteronuclear clusters.[152] It formally involves the homolytic cleavage of the X–X bond in the initial $\mu\text{-}X_2$ complexes and leads to a new way of obtaining mixed metallic clusters.[152,153]

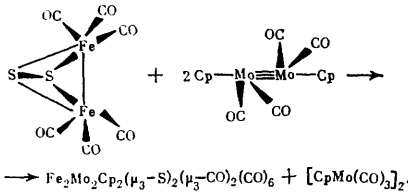
### 13. The Interaction of Compounds (I) with Transition Metal π-Complexes

The interaction of $S_2Fe_2(CO)_6$ with $[(\eta\text{-}C_5H_5)Ni(CO)]_2$ in heptane led to the synthesis in 15% yield of the first iron-nickel cluster in which the sulphur atom at the apex (centre) is symmetrically linked to three metal atoms: $(\eta\text{-}C_5H_5)_2Ni_2Fe(CO)_3S$. Its structure has been confirmed by X-ray diffraction.[154]

The interaction of $S_2Fe_2(CO)_6$ with $(C_5H_5)_2Mo_2(CO)_4$ in toluene at 0 °C has been described.[155] It leads to the formation of the red crystalline dimer $[(C_5H_5Mo(CO)_3]_2$

and red-brown crystals of a new iron–molybdenum sulphur-containing cluster of the "butterfly" type having the composition $Fe_2Mo_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}S)_2(\mu_3\text{-}CO)_2(CO)_6$ and characterised by infrared spectroscopy (Scheme 14):

Scheme 14



$\longrightarrow Fe_2Mo_2Cp_2(\mu_3\text{-}S)_2(\mu_3\text{-}CO)_2(CO)_6 + [CpMo(CO)_3]_2.$

The structure of this cluster has been demonstrated by X-ray diffraction.[155]

The reaction of compound (I) with $R_2Mo_2(CO)_4$, where R = Cp, Cp', or $\eta^5\text{-}CH_3C_5H_4$, leading to new isomeric iron–molybdenum sulphur-containing clusters, has been investigated:[156]

$$S_2Fe_2(CO)_6 + 2\,R_2Mo_2(CO)_4 \rightarrow Cp_2Mo_2(CO)_6 + \\ + R_2Mo_2Fe_2(\mu_3\text{-}S)_2(CO)_6(\mu\text{-}CO)_2 + R_2Mo_2Fe_2(\mu_3\text{-}S)_2(CO)_6(\mu\text{-}CO)_2.$$

The $Cp'_2Mo_2Fe_2(\mu_3\text{-}S)_2(CO)_6(\mu\text{-}CO)_2$ cluster has been analysed by X-ray diffraction.[156]

A new heterotetrametallic cluster $(\eta^5\text{-}C_2H_5)_2Cr_2Fe_2(\mu_3\text{-}CO)_2\cdot(\mu_3\text{-}S)_2(CO)_6$, whose structure has been demonstrated by X-ray diffraction, has been obtained by refluxing $S_2Fe_2(CO)_6$ with $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ for 30 min in a hexane–toluene mixture.[157]

## 14. Catalytic Properties of Clusters (I) and (II)

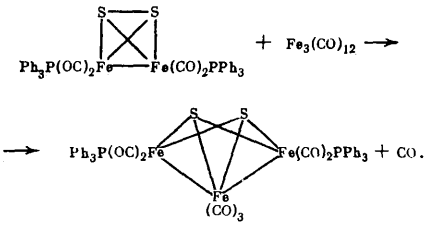
It has been established[3] that cluster (I) and (II) exhibit catalytic activity in the conversion of thiols into disulphides:[158,159]

$$2\,RSH \xrightarrow{\text{(I) or (II)}} RSSR + H_2.$$

This reaction has served as the basis for a new method of eliminating mercaptans from hydrocarbon mixtures.[160] Cluster (II) has a greater catalytic activity in this reaction than cluster (I).

In order to elucidate the causes of the different behaviour of clusters (I) and (II) in the conversion of thiols into disulphides, triphenylphosphine-substituted compounds (I) and (II) were used and their relative activities in the above process were tested. It was found that the monoderivatives of compounds (I) and (II) differ insignificantly in their activities from the corresponding unsubstituted clusters. On the other hand, bis(triphenylphosphine)-substituted clusters (I) virtually lose their ability to convert thiols into disulphides. Steric factors associated with the presence of the bulky triphenylphosphine ligand, which prevents the coordination of the thiol, apparently exert an appreciable influence on the rate of reaction in this case. A different type of behaviour has been observed using a disubstituted derivative of the trinuclear clusters (II) obtained by the reaction of $Fe_3(CO)_{12}$ with a disubstituted derivative of compound (I):

Scheme 15



The activity of the latter cluster is comparable to that of the unsubstituted cluster (II). Bearing in mind the data concerning the interaction of the dinuclear cluster (I) with iron carbonyls and Group IVB elements, obtained by Mavlonov,[3] the $Fe(CO)_3$ cluster is presumably inserted in the S–S bond in this case also.

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The data described above permit the conclusion that the abundance of the reactions of clusters (I) and (II) compared with the mononuclear complexes can apparently be accounted for by the presence of several active centres at the Fe atoms. The activity of tetra- and poly-nuclear clusters is probably still greater.

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During the preparation of the manuscript for the press, a number of studies concerning the synthesis and properties of chalcogeniron carbonyl clusters were published.[161–163]

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# Leukotrienes—Natural Biologically Active Metabolites of Polyunsaturated Acids

R.P.Evstigneeva and G.I.Myagkova

The review deals with the biosynthesis, chemical synthesis, and biological role of leukotrienes—low-molecular-weight bioregulators belonging to the class of eicosanoids—and discusses the prospects for their further investigation and practical application.
The bibliography includes 223 references.

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## I. INTRODUCTION

Polyunsaturated aliphatic acids occupy an important place among natural biologically active compounds. The $C_{20}$ polyenoic acids, namely 5Z, 8Z, 11Z-eicosatrienoic, 8Z, 11Z, 14Z-eicosatrienoic (dihomo-γ-linolenic), 5Z, 8Z, 11Z, 14Z-eicosatetraenoic (arachidonic), and 5Z, 8Z, 11Z, 14Z, 17Z-eicosapentaenoic (timnodonic), synthesised in the living organism from polyenoic acids with a smaller number of carbon atoms such as linoleic, linolenic, etc., are especially important. It has been shown during the last twenty years that polyunsaturated acids are not only structural components of cell membrane lipids, lipoprotein complexes in the brain and spinal cord, the heart, liver, and other organs, but are also precursors of a whole series of their biologically active metabolites—prostaglandins (PG), thromboxanes (TX), leukotrienes (LT), and others, combined under the common name eicosanoids.

The formation of these metabolites in the living cell is based on the enzymic oxidation of polyenoic acids with subsequent conversion into the final compounds. Two pathways leading to the enzymic oxidative transformation of polyenoic acids have now been extensively investigated, especially in relation to arachidonic acid: the cyclo-oxygenase pathway, in which cyclic metabolites of polyenoic acids (prostaglandins and thromboxanes) are formed under the influence of polyenzyme complexes, and the lipoxygenase pathway involving the operation of lipoxygenases and leading to the formation of non-cyclic hydroxyeicosapolyenoic acids and leukotrienes (Scheme 1).[1-9]

Prostaglandins have already been fairly thoroughly investigated and are known as intracellular bioregulators of many physiologically important processes, possessing a wide spectrum of activity on the cardiovascular, respiratory, reproductive, and other systems.[1,2]

Considerable advances have been made in the determination of the structure and in the investigation of the functions of thromboxanes, which are closely related to blood generation processes. Prostacyclin, which is a metabolite of arachidonic acid, has a relaxing effect on the smooth musculature of blood vessels and prevents the clotting processes.[1,2]

Among the acyclic eicosapolyenoic metabolites of arachidonic acid, leukotrienes, whose name was taken from the original source where they were discovered (leukocytes), have attracted special attention. In 1979 the structures of a series of compounds of this class, which are lipid-peptide derivatives exhibiting a high biological activity, were first elucidated. A relation was demonstrated between leukotrienes and the immune and inflammatory processes in the organism, namely its hypersensitivity (various allergic reactions). For this reason, the synthesis and study of the structures and biological activities of leukotrienes, their analogues, and the antagonists and inhibitors of their biosynthesis[2] is of great theoretical and practical interest not only for the recognition of the pathological phenomena in the organism due to the action of leukotrienes, but also for pharmacological purposes, involving the search for effective anti-inflammatory and antiallergic medicinal drugs.[3-9]

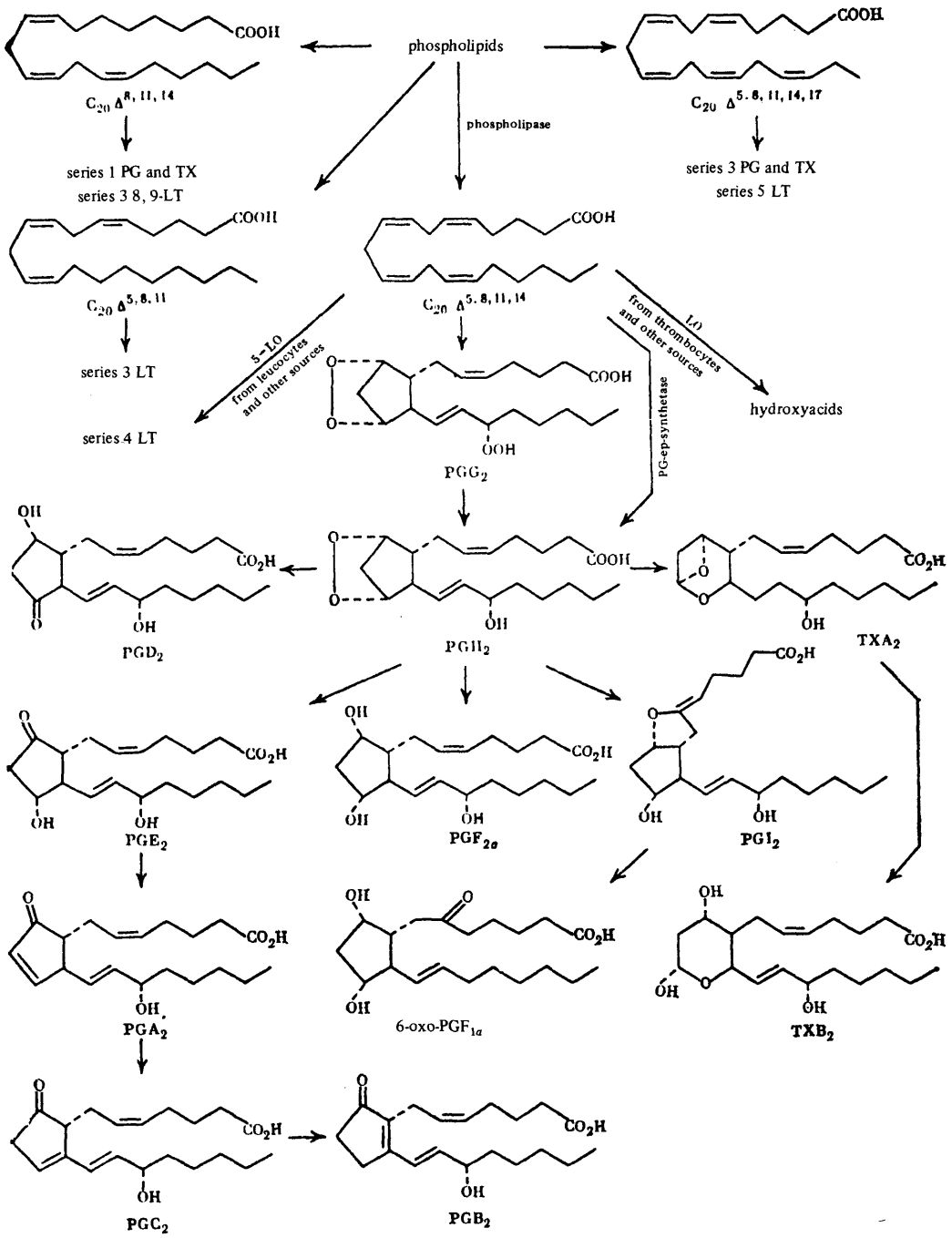
The enormous interest aroused among specialists in various branches of knowledge by the new class of biologically active compounds (leukotrienes) has made it extremely timely to write a review giving a systematic account of data concerning leukotrienes available at the present time.

### 1. The History of the Discovery of Leukotrienes

The lipoxygenase pathway leading to the oxidation of polyenoic acids in leukocytes leads to the formation of leukotrienes (LT)—a new class of biologically active natural metabolites[1-9] (Scheme 2). However, the elucidation of the metabolic pathway leading to the transformation of arachidonic acid into leukotrienes† was preceded by a long history of the discovery and determination of their structure covering a period of 40–80 years.[7,8]

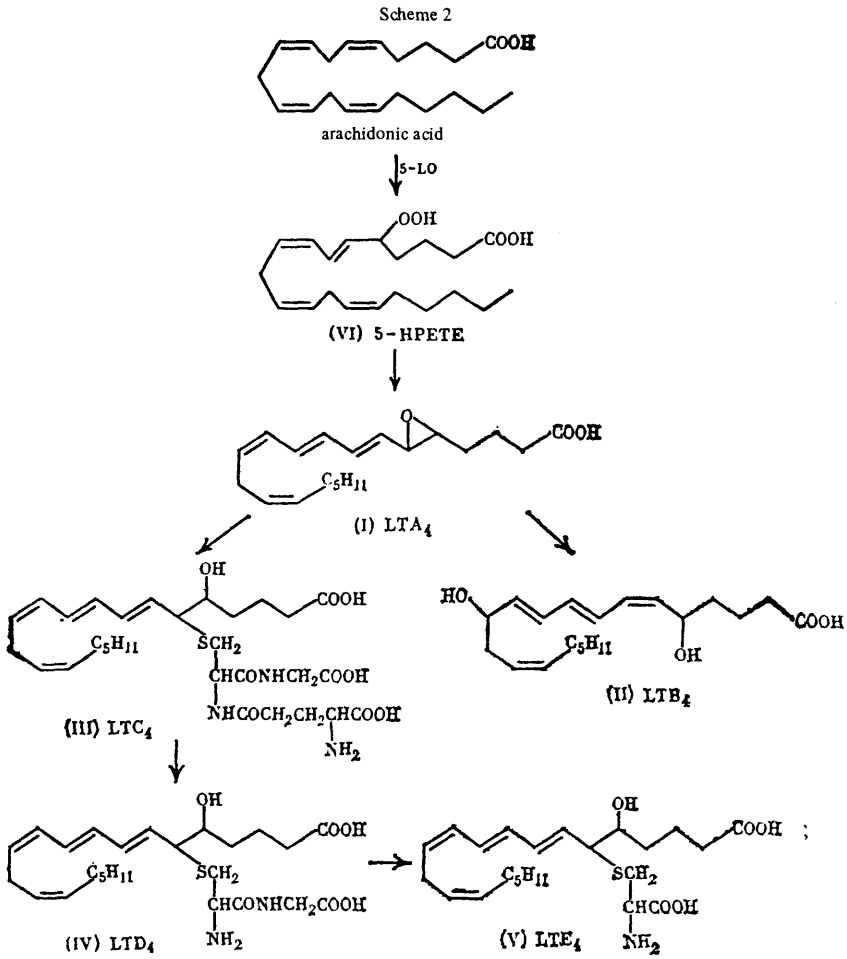
†Leukocytes, the white blood corpuscles, are colourless cells having a nucleus and capable of passing through the walls of blood vessels. They contain proteolytic enzymes and can capture and digest foreign bodies (phagocytosis), performing protective functions in the organism. In terms of their structure, we distinghish granular leukocytes or granulocytes (neutrophils, eosinophils, and basophils) and non-granular leukocytes or agranulocytes (lymphocytes and monocytes).

Scheme 1




Notation: LO = lipoxygenase; PG = ep-synthetase = prostaglandin endoperoxide synthetase.

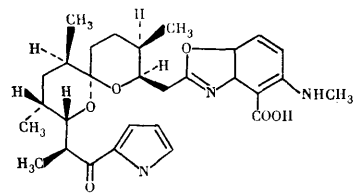
Scheme 2




5-HPETE=Hydroperoxyeicosatetraenoic acid.

A substance isolated from guinea-pig lung tissue on treatment of the latter with cobra venom was described in 1938.[10] A related substance, isolated from the lungs in anaphylactic shock was obtained later.[11]# As a result of its ability to cause a slow contraction of the smooth muscles, this substance has been called the "slow reacting substance of anaphylaxis" (SRS-A)§ to distinguish it from the "slow reacting substance" (SRS) obtained on non-immunological stimulation.

During the ten years following 1950 other sources from which SRS could be isolated were found—various tissues and cell preparations such as the lungs of several species of animals,[13] including human lungs affected by bronchial asthma, cats' paws,[14] the isolated mastocytoma cells¶ from the rat,[15] human leukocytes,[16] and the peritoneal fluid from rats.[17] The possibility of stimulating the isolation of SRS by means of the A23187 calcium ionophore[18] and L-cysteine at a high concentration[19] was demonstrated subsequently.




A23187

#Anaphylaxis (from the Greek ana = against and phylaxis = protection) is a special state with enhanced sensitivity—the hypersensitivity of the organism to the parenteral reintroduction of a foreign non-poisonous protein (for example the blood serum of another animal). The first introduction of a foreign protein (antigen) does not have a pathological effect on the organism but antibodies specific to the given protein introduced into the organism are generated in the latter. If the same protein is reintroduced parenterally after 3 to 4 weeks (when the state of enhanced sensitivity to the given protein has been established, it can persist throughout the life of the organism), severe pathological disorders take place in the organism—anaphylytic shock, which is manifested by a drop of blood pressure, a disorder in cardiac activity, etc. Antigens are substances with characteristic chemical groups which are recognised by the organism as foreign. In response to their introduction into the organism, glycoprotein substances, called antibodies, are generated. They are capable of a specific reaction with antigens.

§SRS-A = slow reacting substance-A (A = anaphylaxis).

¶The mastocytoma cells are tumour mast cells in the connective tissue of vessels characterised by an abundance of basophilic granules.

All the SRS described exhibit an analogous type of biological activity, namely a capacity to cause a strong and prolonged contraction of various types of smooth muscle (the guinea-pig trachaea and human bronchi).[7,8]

During the same years, a growing amount of information confirmed the important functions of the SRS in the enhanced sensitivity reactions of the organism. During the next 20 years many research groups attempted to determine the chemical structure of SRS-A, but major successes were not achieved.

Very promising publications about SRS-A appeared in 1960–1970. On the basis of the results of hydrogenation and oxygenation experiments and also physicochemical properties, it was shown that the SRS is an unsaturated aliphatic acid.[20] A number of investigations[18,21–26] confirmed that arachidonic acid is the initial compound in the synthesis of SRS-A. It has been shown[27] that arachidonic acid stimulates the secretion of SRS from basophilic† leukaemic# rat cells and that 5,8,11,14-eicosatetraynoic acid (an inhibitor of the cyclo-oxygenase component of prostaglandin synthesase as well as lipoxygenase) inhibits the secretion of mediators. It is also extremely important that arachidonic acid, labelled with $^{14}C$ and $^{3}H$, has been incorporated in SRS-A. Consequently it has been shown that SRS-A is a hitherto undescribed product of the metabolism of arachidonic acid.[24]

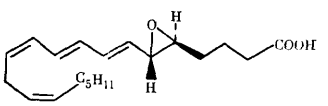
The UV spectrum of the SRS had the characteristic $\lambda_{max}$ = 280 nm, which corresponds to the presence of a ternary conjugated bond system of a non-aromatic chromopore.[28,29] The positions of the double bonds were determined in two ways. Firstly, by the reductive ozonolysis of the SRS biosynthesised from tritium-labelled arachidonic acid with formation of [$^{3}H$]-1-hexanol, which confirms the presence of the $\Delta^{14}$-double bond of the precursor.[30] Secondly, a simple enzymic method involving the use of soya bean lipoxygenase was applied.[31] This enzyme is known to be specific to oxidation at the C(6) atom in aliphatic acids containing the 1*Z*, 4*Z*-diene system, characteristic of linoleic and arachidonic acids, and the accompanying isomerisation of the alkene bond.[32]

The presence of sulphur in the SRS molecules was first mentioned in connection with the study of the mass spectra[33] and was later confirmed by the incoporation of radioactive sulphur on treatment of sensitive guinea-pig lungs with methionine or radioactive sodium sulphate.[34] The fact[35] that cysteine stimulates the formation of the SRS shows that SRS and SRS-A are derivatives of this sulphur-containing aminoacid.[36] The deactivation of SRS-A as a result of treatment with cyanogen bromide confirms the presence of the sulphide bond.[37] The loss of biological activity as a result of brief treatment of SRS-A with acylating and esterifying agents demonstrated the presence of the functional amino- and carboxy-groups.[37]

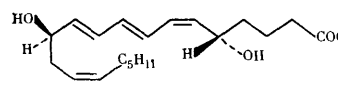
Simultaneously with the study of the structure and role of various slow reacting substances, other groups of investigators discovered that arachidonic acid is metabolised in peritoneal (abdominal) rabbit polymorphonuclear leukocytes.[30–40] Thus, during the last decade there has been a considerable increase in the amount of information available about the biochemical functions of arachidonic acid, which was also assisted by the discovery of prostaglandin endoperoxides, prostaglandins, thromboxanes, prostacyclin,[1–3] and later leukotrienes.[4,8] It was found that the formation of leukotrienes in the living organism is closely related to the appearance of hypersensitive reactions accompanied, as shown previously,[4] by the formation of SRS. This finding as well as structural similarity justified the assignment of SRS to the family of leukotrienes. This was greatly assisted by the major advances in the purification of the SRS, mainly as a result of the application of high-pressure liquid chromatography (HPLC). Morris et al.[28] purified very thoroughly a SRS-A specimen from the guinea-pig lung in a state of anaphylaxis and obtained its UV spectrum, demonstrating the presence of the characteristic absorption bands of leukotrienes. Thus much time and effort by the investigators in many scientific laboratories were needed before Samuelsson, Borgeat, Hammarström, and Murphy[4] reported at the International Congress on Prostaglandins in Washington the completion of studies on the characterisation of the leukotrienes isolated from mouse mastocytoma (tumour) cells and rabbit polymorphonuclear leukocytes (granular). It was also shown that SRS is a set of several leukotrienes, each of which is a $C_{20}$ polyenoic acid with a characteristic system of conjugated double bonds and substituents in various positions in the molecule, among which aminoacids and di- and tri-peptides were found in addition to the epoxy- and hydroxy-groups.[4–10]

## 2. The Nomenclature and Terminology of Leukotrienes

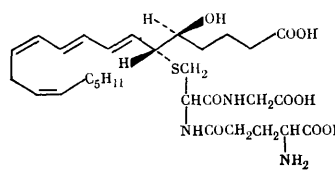
This new class of biologically active natural products was first described in a series of communications[4–8] and represents a set of oxygen-containing aliphatic polyenoic $C_{20}$ acids with various substituents. The compounds were called leukotrienes (LT), since they were first discovered in leukocytes and their structure is characterised by a system of three conjugated double bonds—a conjugated "triene". Owing to the structural differences between the substituents at the 5- and 12-carbon atoms, leukotrienes are divided into groups A, B, C, D, and E. Since leukotrienes are metabolites of 5*Z*, 8*Z*, 11*Z*-eicosatrienoic, 5*Z*, 8*Z*, 11*Z*, 14*Z*-eicosatetraenoic (arachidonic), and 5*Z*, 8*Z*, 11*Z*, 14*Z*, 17*Z*-eicosapentaenoic acids, a digital index (indication of the series) was introduced into the designation of the LT: 3, 4, and 5 respectively, defining the number of double bonds in the leukotriene molecule. The nomenclature and terminology are illustrated in relation to leukotrienes derived from arachidonic acid, since these have been most thoroughly investigated:




5(*S*), 6(*R*)-epoxy-7*E*, 9*E*, 11*Z*, 14*Z*-eicosatetraenoic acid (I)



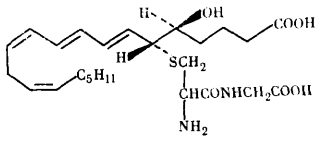

5(*S*), 12(*R*)-dihydroxy-6*Z*, 14*Z*, 8*E*, 10*E*-eicosatetraenoic acid (II)



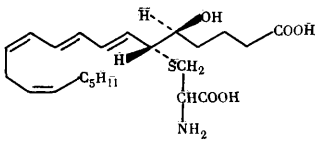

6(*R*)-*S*-glutathionyl-5(*S*)-hydroxy-7*E*, 9*E*, 11*Z*, 14*Z*-eicosatetraenoic acid (III)

†Basophilic cells are a variety of granulocytes (granular leukocytes).

#Leukaemic cells are growing immature forms of leukocytes characteristic of malignant diseases of the blood generation system combined under the common name leukaemia.

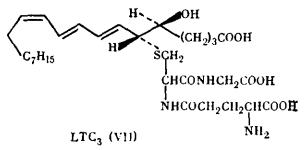


6(*R*)-*S*-cysteinylglycyl-5(*S*)-hydroxy-7*E*, 9*E*, 11*Z*, 14*Z*-eicosatetraenoic acid (IV)

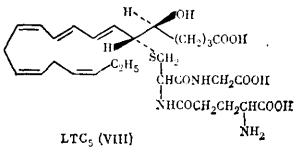


6(*R*)-*S*-cysteinyl-5(*S*)-hydroxy-7*E*, 9*E*, 11*Z*, 14*Z*-eicosatetraenoic acid (V)

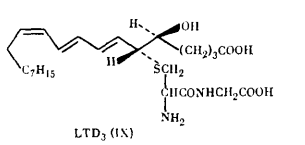
The following metabolites of 5,8,11- and 5,8,11,14,17-eicosapolyenoic acids are known at the present time:[41-44] $LTC_3$—6(*R*)-*S*-glutathionyl-5(*S*)-hydroxy-7*E*, 9*E*, 11*Z*-eicosatrienoic acid (VII); $LTC_5$—6(*R*)-*S*-glutathionyl-5(*S*)-hydroxy-7*E*, 9*E*, 11*Z*, 14*Z*, 17*Z*-eicosapentaenoic acid (VIII); $LTD_3$—6(*R*)-*S*-cysteinylglycyl-5(*S*)-hydroxy-7*E*, 9*E*, 11*Z*-eicosatrienoic acid (IX); $LTD_5$—6(*R*)-*S*-cysteinylglycyl-5(*S*)-hydroxy-7*E*, 9*E*, 11*Z*, 14*Z*, 17*Z*-eicosapentaenoic acid (X); $LTE_3$—6(*R*)-*S*-cysteinyl-5(*S*)-hydroxy-7*E*, 9*E*, 11*Z*-eicosatrienoic acid (XI); $LTE_5$—6(*R*)-*S*-cysteinyl-5(*S*)-hydroxy-7*E*, 9*E*, 11*Z*, 14*Z*, 17*Z*-eicosapentaenoic acid (XII):



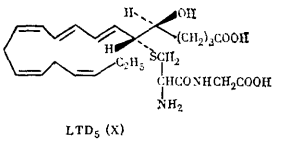
$LTC_3$ (VII)



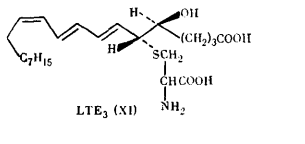
$LTC_5$ (VIII)



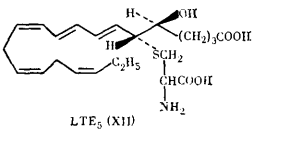
$LTD_3$ (IX)



$LTD_5$ (X)



$LTE_3$ (XI)



$LTE_5$ (XII)

In order to understand the above literature information, it is necessary to note the following points:[8,45] (1) The first component of SRS, characterised as a leukotriene has been the cysteinyl derivative of 5-hydroxy-7,9,11,14-eicosatetraenoic acid designated as LTC. At the present time this compound is referred to as $LTE_4$. (2) The initial studies on the purification of leukotrienes led to the preparation of two isomers relative to the C(11) atom involved in the double bond in the glutathione derivative of 5-hydroxy-7,9,11,14-eicosatetraenoic acid. The principal component was designated by LTC-1 [46] and the minor component by LTC-2. These compounds are referred to nowadays as $LTC_4$ and 11*E*-$LTC_4$ respectively.[45]

In 1983 studies were published demonstrating the conversion of 8*Z*, 11*Z*, 14*Z*-eicosatrienoic (dihomo-γ-linolenic) acid on incubation with A23187 ionophore, which stimulated the mastocytoma cells, into series 3 leukotrienes.[47,48] This led to the isolation of 8,9-$LTC_3$, exhibiting a spasmogenic activity comparable to that of $LTC_3$.[49] It has been suggested that the stoichiometry of 8,9-$LTC_3$ is analogous to that of the metabolites of polyenoic acids when the latter undergo the lipoxygenase oxidation at C(5).

## II. BIOSYNTHESIS AND DETERMINATION OF THE STRUCTURE OF LEUKOTRIENES

The metabolism of arachidonic acid under the influence of lipoxygenase was observed in peritoneal rabbit polymorphonuclear leukocytes. Borgeat et al.[38] incubated arachidonic acid with rabbit leukocytes of the above type and isolated 5(*S*)-hydroxy-6,8,11,14-eicosatetraenoic acid (5-HETE) (XIII) (Scheme 3). Similarly, 8*Z*, 11*Z*, 14*Z*-eicosatetraenoic (dihomo-γ-linolenic) acid is converted into 8(*S*)-hydroxy-9,11,14-eicosatrienoic acid.[48] Another arachidonic acid metabolite, whose structure was determined as 5(*S*),12(*R*)-dihydroxy-6,8,10,14-eicosatetraenoic acid, referred to subsequently as leukotriene $B_4$, was later isolated from rabbit polymorphonuclear leukocytes.[8,50] This was the first arachidonic acid metabilite isolated which contained three conjugated double bonds.[39]

The presence and positions of the two hydroxy-groups at C(5) and C(12) in compound (II) as well as the four double bonds at the 6-, 8-, 10-, and 14-carbon atoms were demonstrated by gas chromatography and mass-spectrometric analysis for a series of derivatives of compound (II).[39,51]

In the study of the metabolism of arachidonic acid in mammalian polymorphonuclear leukocytes,[39,52] the structures of four minor arachidonic acid metabolites were described in addition to $LTB_4$ (Scheme 3). These compounds were 5,6-dihydroxy-7,9,11,14-eicosatetraenoic acids, epimeric at C(6) (XIV, a and b), and two geometrical isomers of leukotriene $B_4$—epimeric at C(12) (XIV, C and D).[52] Although these four compounds probably do not themselves exhibit biological activity, their importance in subsequent studies of the mechanism of the formation of leukotrienes was nevertheless demonstrated.

Experiments showed[40] that, when mammalian polymorphonuclear leukocytes with polymorphic nuclei are incubated with arachidonic acid, the unstable compound (I) is formed, reacting readily with weak nucleophiles—water, ethanol, methanol, etc. Further studies demonstrated that this compound is very labile at low pH but is much more stable in an alkaline medium; its half-life is short (3 min, pH 7.4, $T$ = 37 °C). Other experiments permitted the conclusion that $LTB_4$ is formed in the enzymic hydrolysis of compound (I), while four other dihydroxy acids, namely (XIV, a and b) and (XIV, c and d), are formed from the same compound but as a result of non-enzymic hydrolysis[8,53] via the corresponding intermediates (Scheme 3).

These data suggested that the unstable intermediate 5,6-epoxy-7,9,11,14-eicosatetraenoic acid, subsequently called leukotriene $A_4$($LTA_4$), is formed from 5-hydroperoxy-6,8,11,14-eicosatetraenoic acid (5-HPETE), which is produced by the lipoxygenase oxidation of arachidonic acid.[40]

Corey et al.[54] published a method of chemical synthesis of 5(*S*)-hydroperoxy-6,11,11,14-eicosatetraenoic acid and of its enzymic synthesis by the incubation of arachidonic acid with lipoxygenase isolated from the potato.

The epoxide (I) was isolated from human polymorphonuclear leukocytes.[55] It has also been shown that, under the influence of neutrophils,§ compound (I) ($LTA_4$) is capable of being transformed into $LTB_4$.[53]

The geometry of the double bonds and the configuration of the epoxy-group in $LTA_4$ have been confirmed by specific chemical synthesis of this compound and by the study of the products of its degradation.[56,57] The discovery of the leukotrienes $D_4$ and $C_4$ was associated with the efforts made

§ Neutrophils are a variety of granulocytes (granular leukocytes) (see above).

to establish the structure of the slow reacting substance of anaphylaxis (SRS-A).[3-8] Simultaneously with these investigations by Borgeat and Samuelsson,[30,38,39] some other investigators joined the research into the slow reacting substance. Thus a highly pure SRS-A specimen was obtained by the HELC method from the lung of the guinea-pig in a state of anaphylaxis whose UV spectrum showed clearly the characteristic features of the leukotrienes.[28] Many experimenters have pointed out the special role of arachidonic acid in the synthesis of SRS-A.[18-24,58-60]

It has been shown that many thiols and especially cysteine stimulate the formation of SRS and SRS-A.[30,36] These studies have confirmed that SRS and SRS-A may be suphonated compounds and thus can behave as conjugate compounds in relation to cysteine and leukotrienes $A_4$, which readily react with nucleophiles: thiols and alcohols. In their studies on this hypothesis, Murphy et al.[30] obtained SRS from mouse mastocytoma cells by incubating the latter with arachidonic acid, L-cysteine, and the A23187 ionophore.

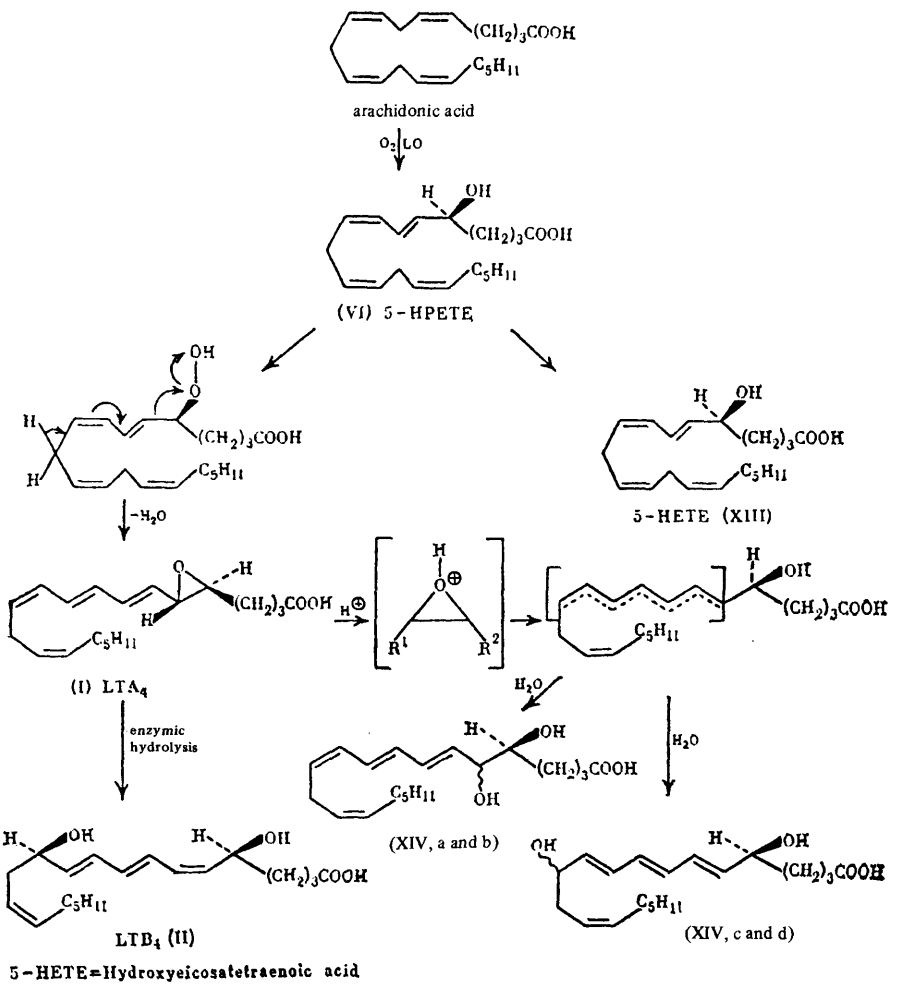
Chemical analyses of the SRS specimen and also of the product of its degradation led to the conclusion that this compound is a derivative of leukotriene $A_4$.

Subsequently the substituent at C(6) in the SRS isolated from mastocytoma mouse cells was identified[61,62] as glutathione ($\gamma$-glutamylcysteinylglycine) and the structure and stereochemistry of the molecule were established by comparing the physicochemical and biological properties of the SRS specimens with a synthetic preparation of known structure.[57] Thus the SRS from the mouse mastocytoma cells was identifed for the first time as 6(*R*)-*S*-glutathionyl-5(*S*)-hydroxy-7*E*, 9*E*, 11*Z*, 14*Z*-eicosatetraenoic acid, which was called leukotriene $C_4$ (Scheme 4).

The role of $LTA_4$ as an intermediate in the metabolism of arachidonic acid has been confirmed by its conversion into $LTC_4$ both by mouse mastocytoma cells and by human polymorphonuclear leukocytes with polymorphic nuclei.[63] However, alternative structures of $LTC_4$ have also been proposed. The possibility of the presence in $LTC_4$ of the 5-hydroperoxy- or peroxyester group has been indicated.[64] Japanese investigators concluded in 1980 that the aminoacid chain is linked to C(6) in $LTC_4$ via a sulpho-group and assumed that this linkage is preferable.[65] The uncertainty concerning the structure of $LTC_4$ was eliminated by the study of the mass spectra and also by chemical synthesis, which confirmed that the natural $LTC_4$ is not a sulphone[66-68] but contains the sulphide bond at C(6).

In 1980 two groups of investigators[69-71] published data concerning the determination of the structure of the SRS

Scheme 3



from basophilic leukaemic cells in the rate, which was identified as 6(*R*)-cysteinylglycyl-5(*S*)-hydroxy-7,9,11,14-eicosatetraenoic acid, called $LTD_4$.

The structure of the SRS from basophilic laukaemic cells of the rat has also been determined by Orning et al.[71], who showed that $LTD_4$ can be obtained by treating $LTC_4$ with γ-glutamyl transpeptidase. This finding shows that $LTC_4$ is an intermediate in the biosynthesis of $LTD_4$ and justifies the assumption that the stereochemistry of the $LTD_4$ molecule is identical with that of $LTC_4$.[71]

It has been shown[70,72] that the SRS-A liberated when sensitive guinea-pig lungs were acted upon immunologically was identical with the SRS secreted by basophilic laukaemic cells of the rat (RBL-I) and was identified as $LTD_4$.[73] The 6-cysteinyl derivative of $LTA_4$ has been found in the SRS-A isolated from peritoneal rat cells.[74] The chemical structure and stereochemistry of this compound have been confirmed by chemical synthesis,[75] which showed it to be 6(*R*)-cysteinyl-5(*S*)-hydroxy-7*E*, 9*E*, 11*Z*, 14*Z*-eicosatetraenoic acid, which has been referred to as $LTE_4$.

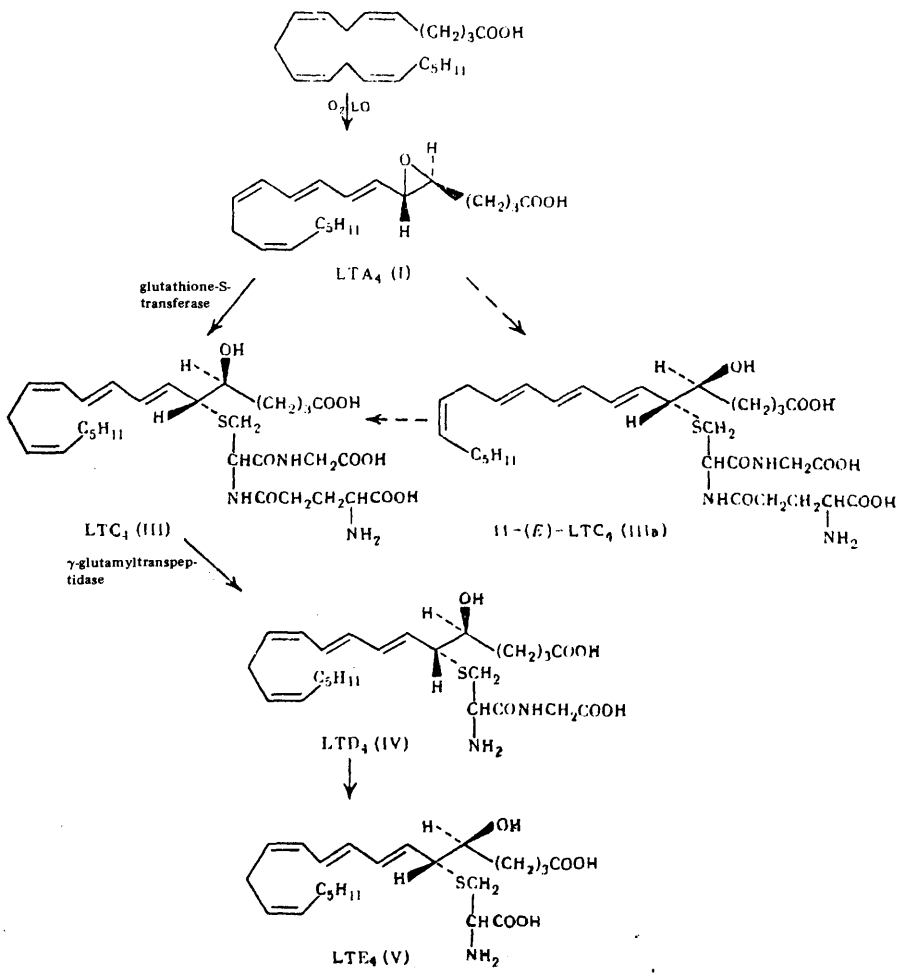
The conversion of $LTA_4$ into $LTC_4$, $LTD_4$, and $LTE_4$ has been frequently confirmed by experiment.[76-80] The bioconversion of $LTC_4$ into $LTD_4$ has also been observed[63] as the enzyme-catalysed removal of the γ-glutamyl residue from $LTC_4$ in the biosynthesis of $LTD_4$.[71] $LTE_4$ has been obtained from $LTD_4$ using the aminopeptidase component of a specific arylsulphatase.[76]

Since leukotrienes are transformed in the $LTC_4 \rightarrow LTD_4 \rightarrow LTE_4$ metabolic cascade, it is not surprising that the composition of any SRS depends on the source, material, and methods used in its isolation. It has been suggested that the term leukotriene be used for an individual compound and the term SRS be applied to the description of material obtained biologically in which the relative amounts of the leukotrienes present are unknown.

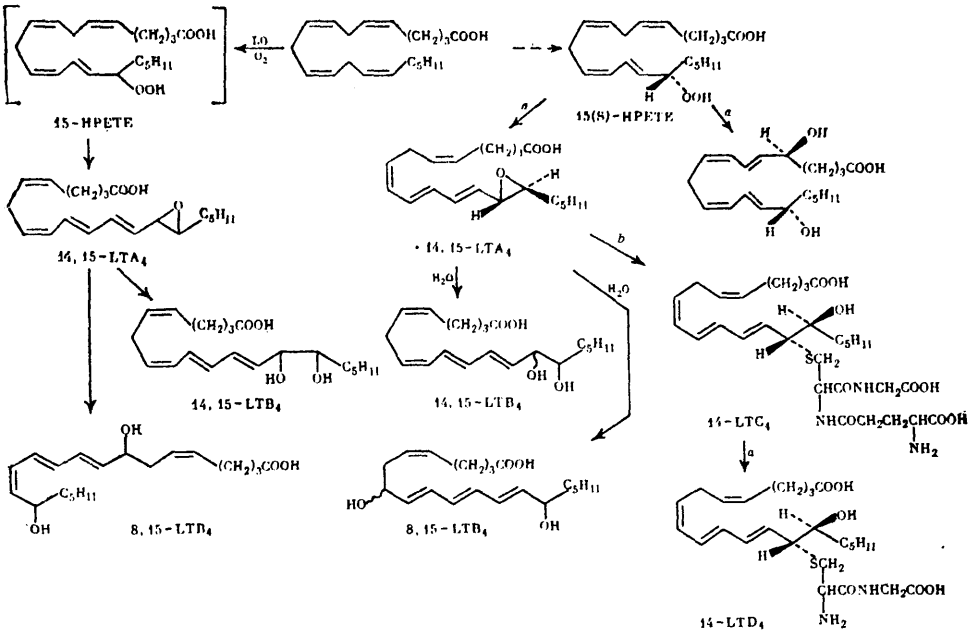
The products obtained from 5-HPETE derived from arachidonic acid are not all confined to leukotrienes (Scheme I). Incubation of arachidonic acid with human leukocytes gives gise to a whole series of metabolites[81-86] which are positional isomers of natural leukotrienes (Scheme 5). Incubation of arachidonic acid with cytochrome P-450 [87] and with the fluid from adrenal cortex[88] leads to product of its oxidation at C(9) and at C(9) and C(15) respectively, which exhibit a high biological activity and are of great interest.[89]

Leukotrienes derives from 4*Z*, 8*Z*, 11*Z*-eicosatrienoic acid and 5*Z*, 8*Z*, 11*Z*, 14*Z*, 17*Z*-eicosapentaenoic acid have also been described in the literature.[41-45] Data have been published concerning the 8,9-$LTC_3$, whose biosynthesis has been achieved by incubating 8*Z*, 11*Z*, 14*Z*-eicosatrienoic (dihomo-γ-linolenic) acid.[47,48]

Scheme 4



Scheme 5



(a) metabolism in human leukocytes;
(b) metabolism in basophilic leukaemic rat cells.

## III. CHEMICAL SYNTHESIS OF LEUKOTRIENES

The first total synthesis of leukotriene $A_4$ was carried out by Corey and published in 1979.[56,90] The syntheses of virtually all the known leukotrienes, their isomers, and their analogues, including isotopically labelled compounds, have now been achieved.

The synthetic studies have been concerned mainly with series 4 leukotrienes ($LTA_4$, $LTC_4$, $LTD_4$, $LTE_4$, $LTF_4$, and $LTB_4$), i.e. leukotrienes whose precursor is arachidonic acid.

The synthesis of the leukotrienes which have been developed are based on the Wittig reaction, whereby one can condense the key fragments in the synthesis—the "carboxyl-containing" fragment from the C(1) atom in the leukotriene molecule and the "hydrocarbon" fragment ranging up to the C(20) atom. The length of the hydrocarbon chain, the degree of unsaturation, and the functional substituents at the 5- and 6-carbon atoms can be varied in each of these fragments for $LTA_4$, $LTC_4$, $LTD_4$, etc. and at C(12) for $LTB_4$.

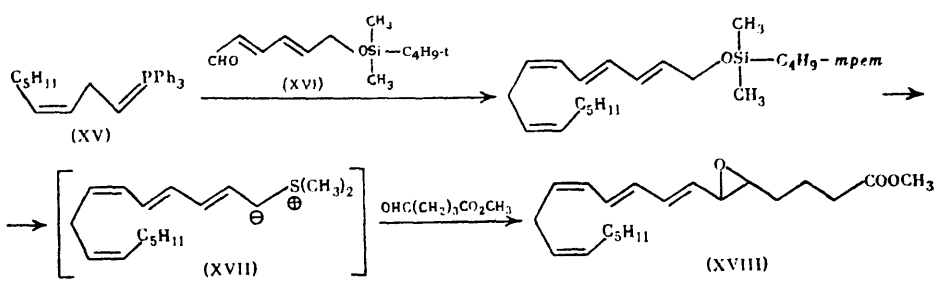
### 1. The Synthesis of Leukotriene $A_4$, Its Isomers, and Its Analogues

The earliest of the known syntheses is that of (±)-$LTA_4$ [56,90,91] involving the Wittig interaction of the monoene fragment (XV) and the diene fragment (XVI) with susequent addition of the hydrocarbon chain in the sulphonium ylide (XVII) and the introduction of the epoxy- and carboxy-groups (Scheme 6).

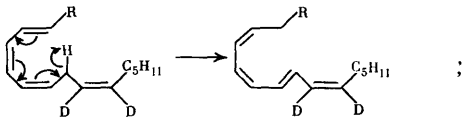
The methyl ester of $LTA_4$ (XVIII) has been obtained in the form of a 1 : 1 mixture of the *cis*-epoxide and the natural *trans*-epoxide.

Rokach et al.[92] have also used the sulphonium ylide (XVII) in the synthesis of the methyl ester of (±)-$LTA_4$ and succeeded in resolving the mixture of the *cis*- and *trans*-epoxides. The same group of investigators[92] attempted to synthesise 9Z-$LTA_4$ because the geometry of the $\Delta^{9,10}$-double bond in the natural leukotriene was unknown at the time. However, the immediate tetraene (XIXa) underwent the 1,7-hydrogen migration at 18–25 °C, affording the isomer

Scheme 6



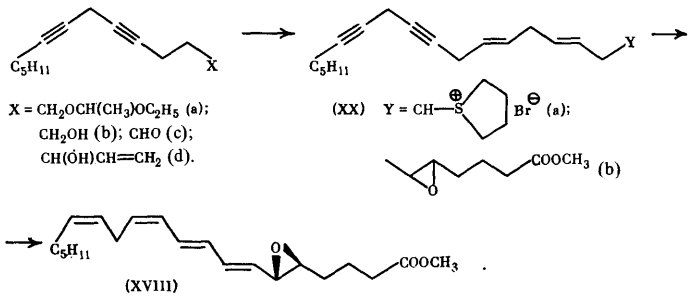
(XIX):



(XIXa) (XIX)

R = $COOCH_3$, $CH_2OH$ .

The methyl ester of (±)-$LTA_4$ was also synthesised by the selective reduction of the diyne (XXb) obtained from the salt (XXa):[93,94]



X = $CH_2OCH(CH_3)OC_2H_5$ (a); $CH_2OH$ (b); CHO (c); $CH(OH)CH{=}CH_2$ (d).

(XX) Y = $CH{-}S^{\oplus}Br^{\ominus}$ (a);

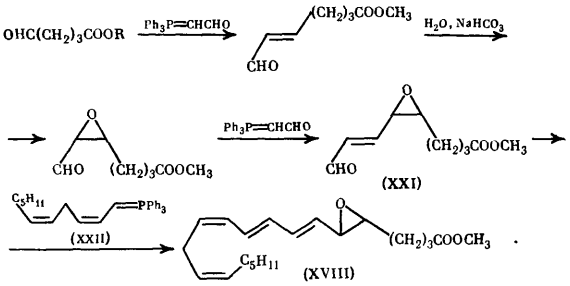
(b)



(XVIII)

Subsequently investigators used in the synthesis of $LTA_4$ schemes providing for the Wittig condensation of the hydrocarbon and carboxyl-containing fragments in the last stages of the synthesis after the preliminary introduction of the necessary functional groups into each fragment. The epoxyaldehyde (XXI), obtained by a series of stages from 4-formylbutyrate, has been used as the key synthone for the introduction of the carboxyl-containing unit[95,96] (Scheme 7). The undecadiene ylides (XXII),[95,96] prepared from phosphonium salts, are employed as the hydrocarbon fragment. The Z-configuration of the double bonds in compound (XXII) is due to the stereospecific hydrogenation of the corresponding acetylenic precursors. The interaction of compounds (XXI) and (XXII) yields the methyl ester of (±)-$LTA_4$ [95] (Scheme 7).

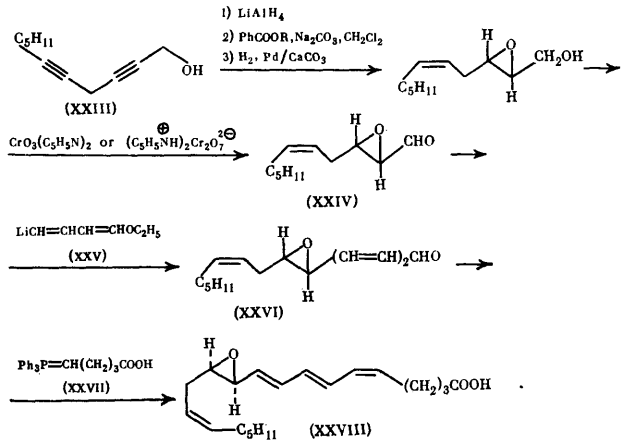
Scheme 7



Gleasson et al.[95] identified the methyl ester of (±)-$LTA_4$ which they synthesised as a 2:1 mixture of the natural 9*E*-compound and the isomeric 9*Z*-compound. The 1,7-hydrogen shift, noted by Rokach et al.[92] (see above), occurred also in the formation of 9*Z*-$LTA_4$.[96]

The triene component (XXVI) has been used as the hydrocarbon fragment in the syntheses of the 11,12-epoxides (XXVIII), which are analogues of the $LTA_4$ (Scheme 8), but, in contrast to the syntheses discussed above, this compound is not an ylide but an aldehyde (Scheme 8).[97] The initial undeca-2,5-diyn-1-ol (XXIII), obtained from acetylene and its derivatives, was converted into the aldehyde (XXIV) via a series of stages.

Scheme 8



The length of the epoxyaldehyde (XXIV) is increased using 4-ethoxy-1-lithio-butadiene (XXV) as the four-carbon component.¶ The conversion of carbonyl compounds into conjugated dienes with the aid of compound (XXV) has been suggested[98] and has been used by other workers to generate an analogous system of multiple bonds in carboxyl-containing components in the synthesis of the 7-*cis*-isomers of $LTA_4$ and $LTD_4$.[99] Subsequently the aldehyde (XXVI) is condensed with the ylide (XXVII) to form the 11,12-epoxy-analogue of $LTA_4$ (XXVIII).

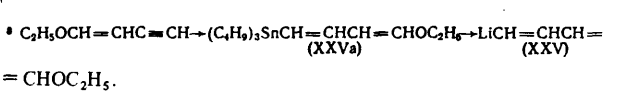
None of these syntheses described previously allowed the selective formation of the natural enantiomer of $LTA_4$. In order to solve this problem, the methyl ester of 5(*S*),6(*R*)-epoxy-6-formylhexanoic acid (XXX), which is synthesised from carbohydrates[100–105] or from carbohydrate derivatives[103,104] containing chiral centres in the molecule, has been suggested as the key compound. Corey et al.[100] (Scheme 9) described the synthesis of the aldehyde (XXX) from 2,3,5-tribenzoyl-D-ribose with its subsequent conversion by the Wollenberg method,[98,99] using 4-ethoxy-1-lithiobutadiene, into the 7*E*, 9*E*-C(1)-C(14) fragment (XXXI), whose interaction with the phosphorane (XXXII), obtained from acetylene,[56,90,92,99–106] gives rise to the enantiomerically individual methyl ester of 5(*S*),6(*S*)-$LTA_4$. The stereochemistry of this compound has been confirmed by its enzymic conversion into the natural $LTB_4$.[53]

The 5(*S*),6(*R*)-epoxyester (XXX) has also been converted into a mixture of the methyl esters of 9*Z*-$LTA_4$ and $LTA_4$.[100] The 11*E*-isomer of $LTA_4$ has been prepared from the 5(*S*),6(*R*)-epoxyester (XXX) by the *trans*-olefination method via the Wittig reaction[45,101] analogously to Scheme 9.

It has been suggested that D-glyceraldehyde acetonide (XXXIII), obtained from D-mannose and L-glyceraldehyde acetonide (XXIV), which was derived in its turn from L-arabinose, be used as the asymmetric precursor in the synthesis of the 5(*S*),6(*R*)-epoxyester (XXX) [105] (Scheme 10).

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¶

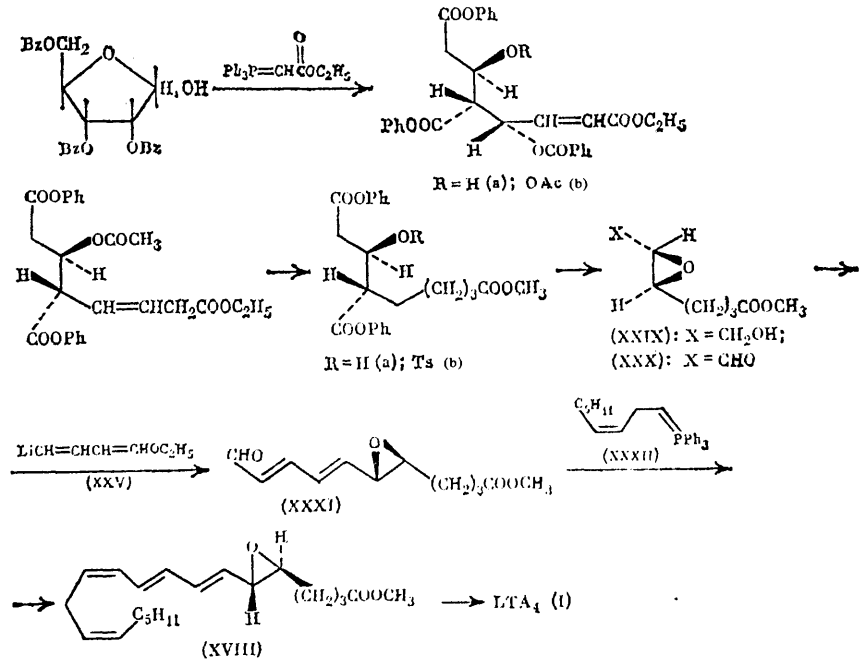


(XXVa) (XXV)

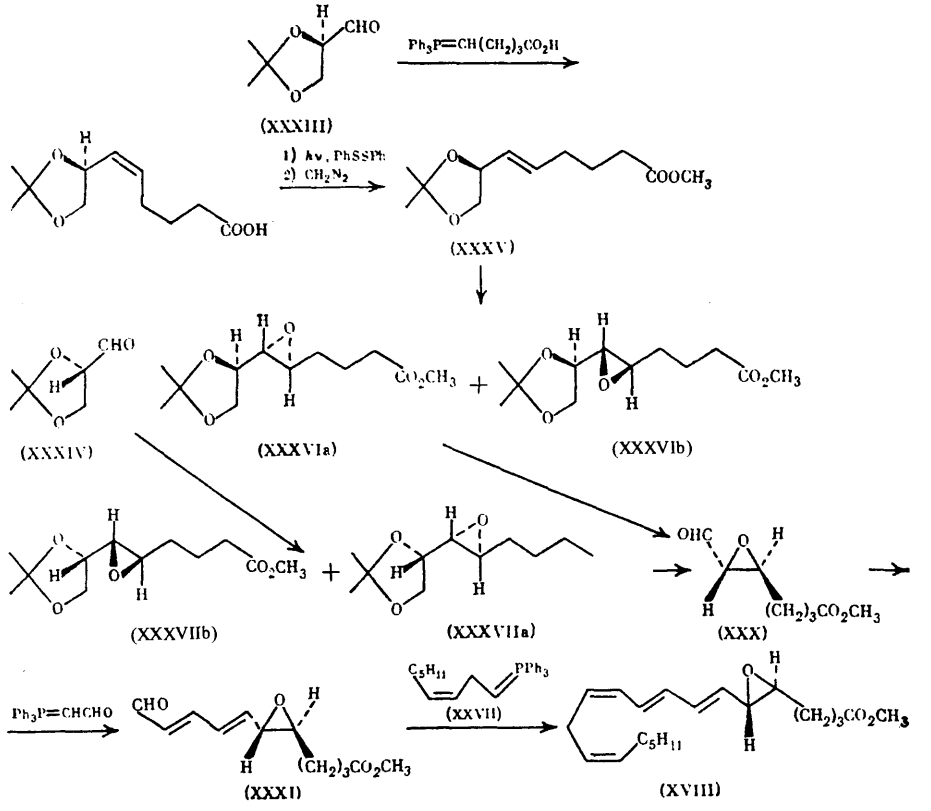
$= CHOC_2H_5$.

The hydrostannylation of 1-ethoxybut-1-en-3-yne yields vinyl stannate (XXVa), whose *trans*-metallation with n-butyllithium yields 4-ethoxy-1-lithiobutadiene (XXV).[98]

Scheme 9



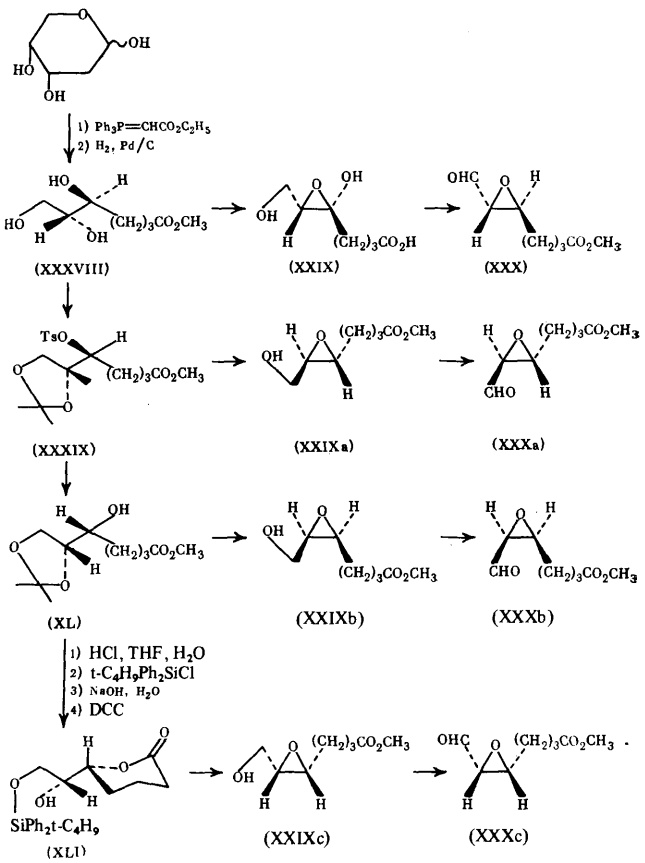
Scheme 10



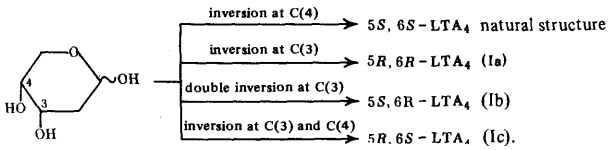
The conversion of the acetonide (XXXIII) into the ester (XXXV) with subsequent epoxidation of the double bond yields a 1:2 mixture of the epoxyesters (XXXVIa) and (XXXVIb) with the preferential formation of the isomer (XXXVIb) having the unnatural stereochemistry of the substituents at the C(5) and C(6) atoms. The epoxide (XXXVIIa) is formed preferentially from L-glyceraldehyde acetonide (XXXIV). The hydrolytic cleavage of both diastereoisomers, (XXXVIa) and (XXXVIIa), leads to the 5(*S*),6(*R*)-formyl ester (XXX), which is converted by three consecutive Wittig reactions into the methyl ester 5(*S*),6(*S*)-$LTA_4$. The 5(*S*),6(*S*)-stereoisomer (XXXb) is synthesised from the acetonides (XXXVIb) and (XXXVIIb).[105]

Using D-2-deoxyribose, Rokach et al.[106] later developed new stereospecific methods of synthesis of the 5(*S*),6(*R*)-, 5(*R*),6(*S*)-, 5(*S*),6(*S*)-, and 5(*R*),6(*R*)-stereoisomers of the aldehydoepoxyester (XXX) and on this basis obtained the natural $LTA_4$: the 5(*S*),6(*S*)-epimer and the 5-epi,6-epi-5(*R*),6(*R*)-, 6-epi,5(*S*),6(*R*)-, and 5-epi-5(*R*),6(*S*)-isomers of $LTA_4$ [compounds (Ia), (Ib), and (Ic) respectively] in the form of their methyl esters (XVIII), (XVIIIa), (XVIIIb), and (XVIIIc) respectively. In these studies, the authors took into account the disadvantage of using D-ribose in such syntheses,[100,102] consisting in the fact that the hydroxy-group at the C(2) atom had to be removed by reductive elimination, which entailed additional complications as regards the protection of the hydroxy-group at the C(4) atom, and developed the syntheses from D-2-deoxyribose.

Scheme 11



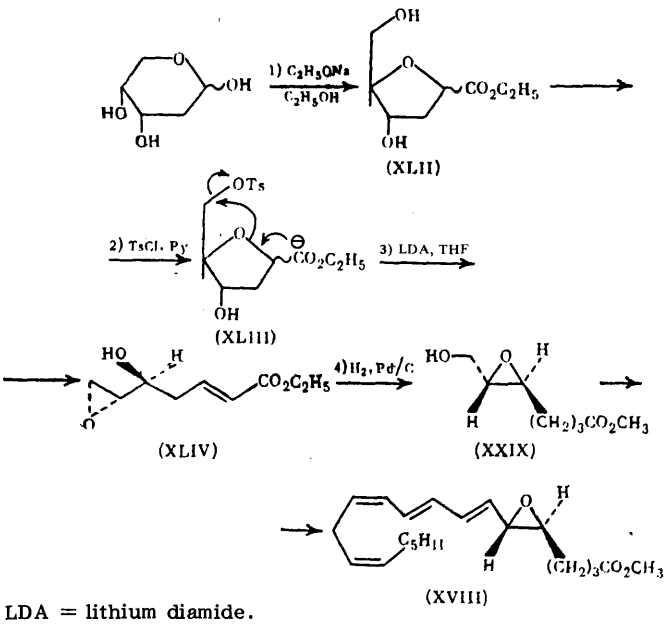

The main strategy used in these syntheses involved the appropriate manipulations of the chiral centres at the C(3) and C(4) atoms in D-2-deoxy-D-ribose in such a way that these two centres become chiral centres at the C(5) and C(6) atoms in the leukotrienes (I), (Ia), (Ib), and (Ic) synthesised, which can be represented schematically in the following way:




2-Deoxy-D-ribose is converted by a series of consecutive chemical reactions[106] into the triol (XXXVIII), the acetals (XXXIX) and (XL), and the lactone (XLI). Each compound obtained is a precursor of the diastereoisomeric epoxy-alcohols (XXIX), (XXIXa), and (XXIXb), (XXIXc), which are then oxidised[97] to the 5(*S*),6(*R*)-, 5(*R*),6(*S*)-, 5(*S*),6(*S*)-, and 5(*R*),6(*R*)-epoxyaldehydes [(XXX), (XXXa), (XXXb), and (XXXc) respectively] (Scheme 11).

The diastereoisomeric aldehydes (XXX), (XXXa), (XXXb), and (XXXc) obtained in this way by means of three consecutive Wittig olefination reactions,[105,106] as described above, are converted into the ethyl esters of $LTA_4$ (XVIII), 5-epi,6-epi-$LTA_4$ (XVIIIa), 6-epi-$LTA_4$ (XVIIIb), and 5-epi-$LTA_4$ (XVIIIc) respectively.[106]

Another method in which 2-deoxy-D-ribose is used to synthesise the epoxyesters (XXIX), (XXIXa) and (XXIXc) has been proposed.[107] It is based on the conversion of 2-deoxy-D-ribose into the *C*-glycoside (XLII)[108,109] with subsequent initiation of the intramolecular reaction of the tosylate (XLIII), leading to the formation of the epoxy-compound (XLIV), which is readily converted into the primary alcohol (XXIX) from which the methyl ester of $LTA_4$ is obtained after a series of known stages:

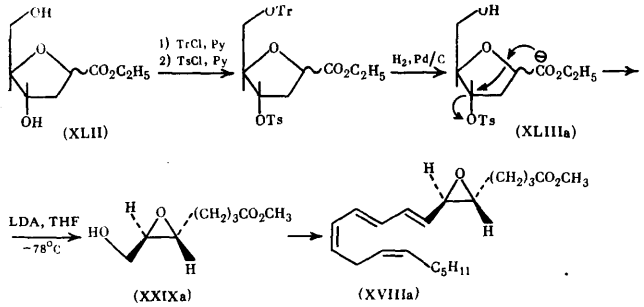



LDA = lithium diamide.

14,15-dehydro-$LTA_4$ has also been obtained from the hydroxyester (XXIX).[66,110]

The use of the tosylate (XLIIIa) leads to the inversion of the configuration at C(5) in the glycoside and the formation of the hydroxyester (XXIXa), which is converted further

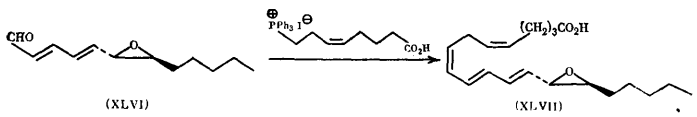
into the ester of 5-epi,6-epi-LTA$_4$:



The synthesis of the hydroxyester (XXIXc), a precursor of the ester of 5-epi-LTA$_4$, involves the inversion of the configuration of the secondary hydroxy-group of the *C*-glycoside (XLII) and the tosylation of the primary hydroxy-group in compound (XLV), as shown in Scheme 12.

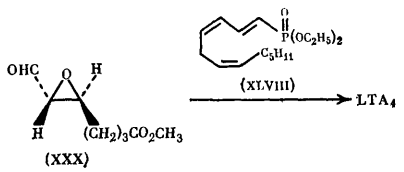
Simultaneously with the studies by Rokach and co-workers,[106,107] Mariotti and Bentick[111] proposed a somewhat modified synthesis of the epoxyalcohol (XXIX) also on the basis of 2-deoxy-D-ribose.

2-Deoxy-D-ribose has been used successfully in the synthesis of the epoxyaldehyde (XLVI),[112] from which 14(*S*),15(*S*)-epoxy-5*Z*, 8*Z*, 10*E*, 12*E*-eicosatetraenoic acid 14,15-LTA$_4$ (XLVII) was obtained by a standard method:[107,112]

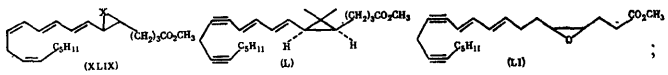


The methyl ester of 5(*S*),6(*S*)-epoxy-7-hydroxyheptanoic acid (XXIX) and its 5(*S*),6(*R*)-diastereoisomer (XXIXb), which are precursors of LTA$_4$ and 6-epi-LTA$_4$, have also been synthesised from 2,3-*O*-isopropylidene-D-erythrose[113] and 5(*S*),6(*S*)-epoxyaldehyde (XXXb) has been obtained from bis-isopropylidene-D-(+)-mannose.[114]

A synthesis of LTA$_4$ in which the phosphonates (XLVIII) were used instead of the phosphonium salts as the C(13) to C(20) fragment was published in 1982:[115]



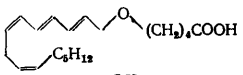
The diacetylene analogue (XLVIII) was used in the synthesis of the methyl ester of (±)-LTA$_4$.[116] A phosphonate, whose structure resembled that of compound (XLVIII), has also been used to synthesise the methyl ester of 5,6-methanoleukotriene A$_4$ (XLIXa) [117,118] (a stable biologically active analogue of LTA$_4$), bisdehydrodimethylmethanoleukotriene A$_4$ (L),[119,120] and a bisdehydro-analogue of LTA$_4$ (LI):[120,121]



X = $CH_2$ (a); S (b); N (c).

A thio-analogue of LTA$_4$ (XLIXb) has been prepared by the same methods.[120] An aza-analogue of LTA$_4$ (XLIXc) has been synthesised[123] using 5-epi,6-epi-LTA$_4$.[106] The acetylenic analogues of LTA$_4$ serve as the initial compounds for the synthesis of tritium-labelled leukotrienes.[123,124]

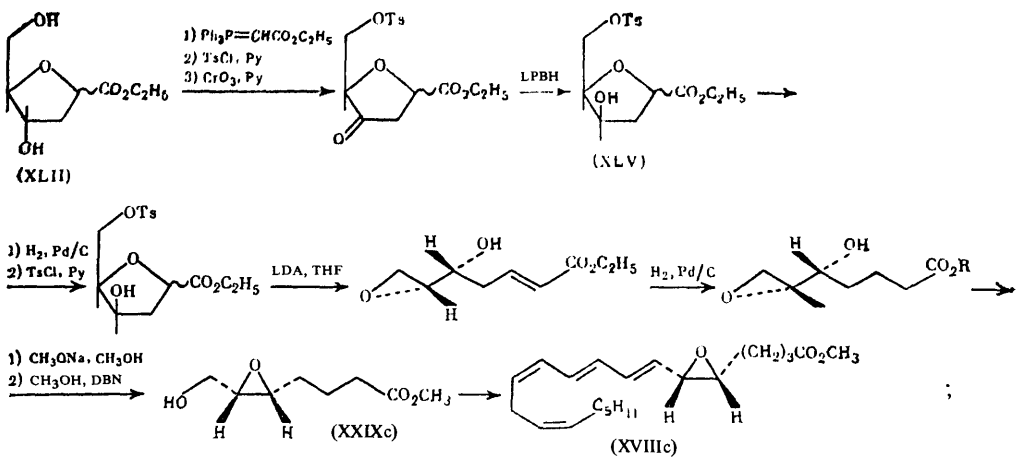
6-Oxa-8*E*, 10*E*, 12*Z*, 15*Z*-eicosatetraenoic acid, secoleukotriene A$_4$ (LII), whose synthesis has been published recently,[125,126] is also an analogue of LTA$_4$.



(LII)

The syntheses of LTA$_4$ using initial chiral compounds (carbohydrates and their derivatives) [100–114] involve many stages and require a large number of protecting operations and the removal of various groups to ensure the inversion of substituents at the initial chiral centres to give the configuration characteristic of the leukotriene structure. The stereospecific oxidation of achiral alcohols by a reagent comprising diethyl L-(+)-tartrate, t-butyl hydroperoxide,

Scheme 12



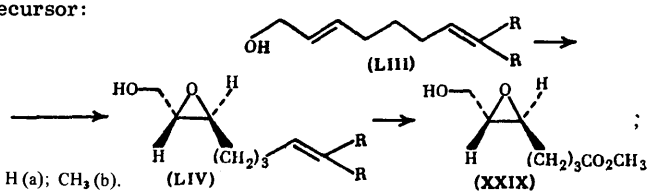
LPBH = lithium perhydro-9B-boraphenylallyl hydride;
DBN = 1,5-diazabyclo[4,3,0]non-5-ene.

and tetraisopropoxytitanium, proposed by Katsuki and co-workers,[127,128] has been a major advance in the methology of the synthesis of leukotrienes.

However, there is evidence that methyl 7-hydroxy-5-heptenoate



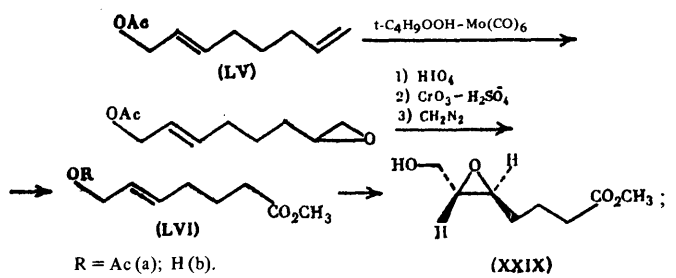
is epoxidised under these conditions with low yields.[103,127,128] At the same time, two research groups developed the selective epoxidation of the diene alcohols (LIIIa) [128] and (LIIIb).[103] The oxidative cleavage of the alkene structure of the epoxide (LIV) with subsequent esterification gives rise to the 5(*S*),6(*S*)-epoxyalcohol (XXIX) as the $LTA_4$ precursor:



R = H (a); $CH_3$ (b).

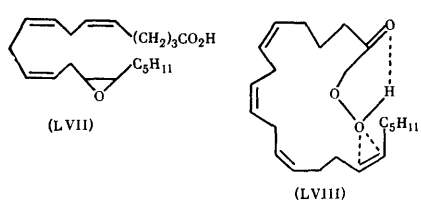
The epoxide (XXIX) has been synthesised[120,129] from 1-acetoxy-2*E*,7-octadiene (LV) by the chiral epoxidation of methyl 7-hydroxy-5*E*-heptenoate (LVIa) or its acetate (LVIb) using the Sharpless–Katsuki method (Scheme 13):

Scheme 13



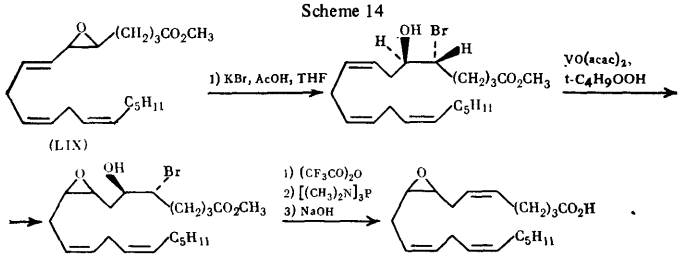
R = Ac (a); H (b).

This method[127,128] has been used also in the synthesis of 8,9-$LTA_3$.[47,130] Corey and co-workers[131–133] achieved the selective epoxidation of the double bond nearest to ($\Delta^{5,6}$) and most remote from ($\Delta^{14,15}$) the carboxy group in arachidonic acid. The 14,15-epoxide (LVII) has been synthesised by the novel intramolecular transfer of oxygen in peroxyarachidonic acid, which isomerises preferentially via the intermediate (LVIII):



8,8-Epoxyarachidonic acid (LIX) has been synthesised from the methyl ester of the 5,6-epoxyacid (LX),[87,134] (Scheme 14):

Scheme 14



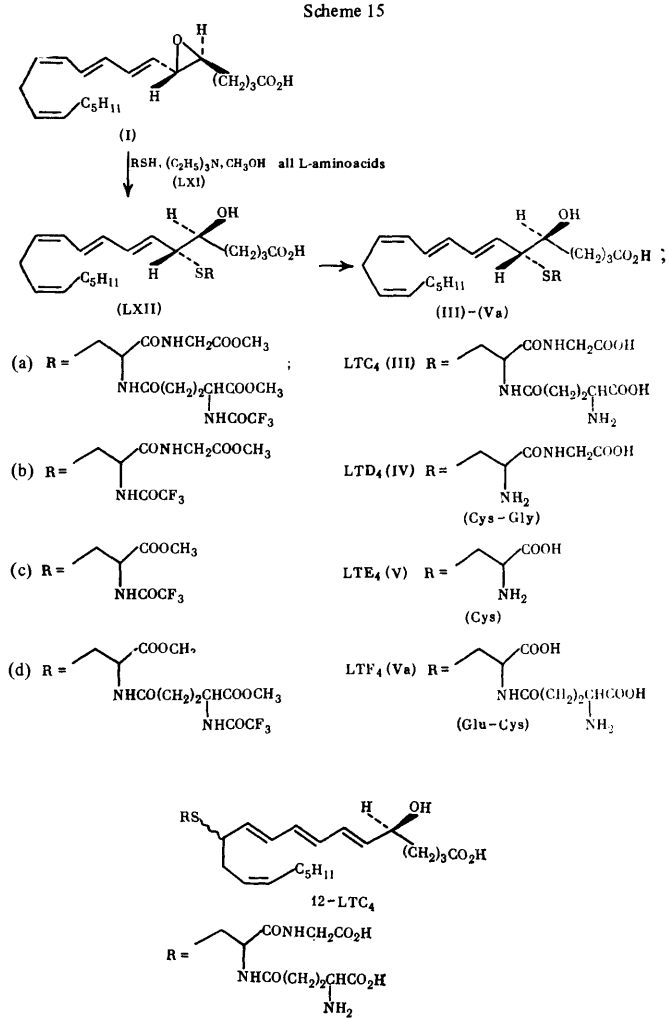
Compound (LX) has also been isolated from natural sources.[87]

A biospecific synthesis of the methyl ester of $LTA_4$ from 5-HPETE (VI) is known.[46,135–137] Other natural epoxides have also been obtained by biospecific synthesis.[112,136]

## 2. The Syntheses of the Leukotrienes $C_4$, $D_4$, $E_4$, and $F_4$, Their Isomers, and Their Analogues

The syntheses of $LTC_4$,[92–97,100–105,111,124,128–132,136–142] $LTD_4$,[92–105,114,124,130–142] $LTE_4$,[93,94,100,103,105,124,140–143] $LTF_4$,[94,143] their isomers, and their analogues[93,96,102,111,124,139–144] are based on the introduction in the 6-position in the $LTA_4$ molecule of the thio-derivatives (LXI), whose role is assumed by the corresponding protective aminoacids and peptides in $LTA_4$ [100,105] (Scheme 15).

Scheme 15

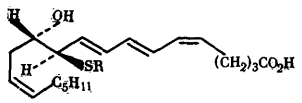


The removal of protecting groups from compounds (LXII, a–d), depends on the nature of the peptide substituent. There are data concerning the addition of glutathione in the unprotected form.[57,61,62,119–121,135] Hydroquinone, which is an essential component in the hydrolysis of the $LTE_4$ esters, leads to the partial isomerisation of the double bond in the 11-position in leukotrienes.[75] The use of an excess of lithium perchlorate when it is necessary to alter the direction of the $LTC_4$ formation reaction leads to the synthesis of 12-glutathionylleukotrienes (12-$LTC_4$),[102] which exhibit an extremely low biological activity and apparently do not make a significant contribution to the biological role of the members

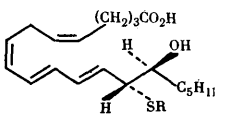
of the family of leukotrienes. This finding is important for the elucidation of the structure of the SRS components.[145]

The recently isolated $LTF_4$ (Va) has been synthesised by means of Scheme 15 described above from $LTA_4$ and protected glutamylcysteine.[134] The compound has been obtained in a mixture with its 5(*R*),6(*S*)-diastereoisomer and proved to be 200 times less active in its effect on human bronchi than $LTD_4$.[143] The 5(*R*),6(*S*)-diastereoisomers of $LTC_4$, $LTD_4$, and $LTE_4$ were synthesised in the same investigation.[143] Their biological activities proved to be lower by two orders of magnitude than that of the natural product. Other $LTC_4$, $LTD_4$, and $LTE_4$ diastereoisomers have also been synthesised.[61,111,114]

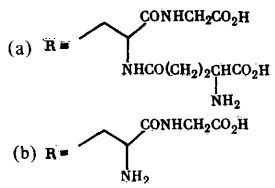
11-Glutathionyl- [11-$LTC_4$ or (LXIIIa)], 11-cysteinylglycyl- [11-$LTD_4$ or (LXIIIb)], 14-glutathionyl-$LTC_4$ [14-$LTC_4$ or (LXIVa)], and 14-cysteinylglycyl-leukotrienes [14-$LTD_4$ or (LXIVb)] have been synthesised from 11,12- and 14,15-epoxy-analogues of $LTA_4$ and protected peptides. These leukotrienes are positional analogues of the natural $LTC_4$ and $LTD_4$.[97]



(LXIII)



(LXIV)

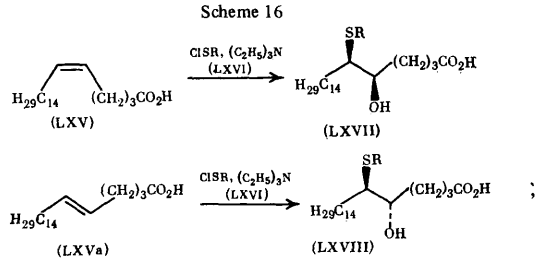


The 7-*cis*-isomer of $LTD_4$, whose activity amounted to one-tenth of that of the natural $LTD_4$, has been obtained by the same method.[99]

It has been suggested that the *S*-trimethylsilyl derivatives [R-S-Si$(CH_3)_3$] of the *N*-trifluoroacetylglutathione and *N*-trifluoroacetyl-L-cysteine esters be used in the synthesis of $LTC_4$ and $LTE_4$.[92]

The stereoisomers of fully saturated octahydro-analogues of the leukotrienes $C_4$ [(LXViia) and (LXVIIIa)], $D_4$ [(LXVIIb) and (LXVIIIb)], and $E_4$ [(LXVIIc) and (LXVIIIc)] have been synthesised[139,140] by the stereoselective interaction of sulphenyl halides (LXVI) with the 5*E*- and 5*Z*-eicosenoic acids (LXVa) and (LXVb) (Scheme 16):

Scheme 16

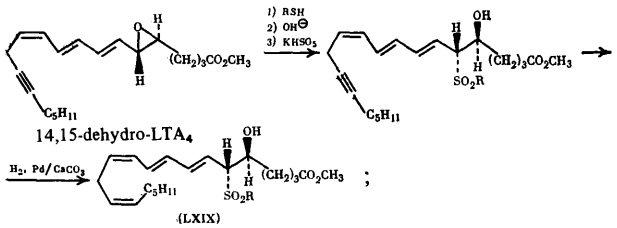


(a) R = glutathione; (b) R = Cys–Gly; (c) R = Cys.

9*Z*- and 9*Z*, 11*E*-$LTC_4$ have been synthesised from $LTA_4$ isomers with known stereochemistry.[138]

The 11*E*-isomer of $LTC_4$, isolated previously from mastocytoma cells,[30] has been synthesised from 11*E*-$LTA_4$ and glutathione.[68,101]

The uncertainty of the state of oxidation of the thio-bond in the natural $LTC_4$ in the determination of its structure (LXVII) made it essential to synthesise the $LTC_4$ sulphone (LXIX):



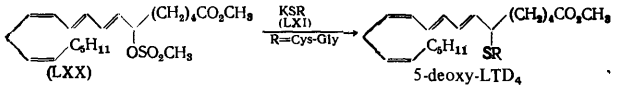
14,15-dehydro-$LTA_4$

(LXIX)

R = glutathione.

Comparison of the physicochemical and biological properties of the sulphone (LXIX) with those of the natural $LTC_4$ confirmed the presence of the sulphide linkage in the latter.[66,67]

The study of the molecular binding of leukotrienes and the determination of the structure of the possible receptor led to the problem of the synthesis of 5-deoxy-$LTD_4$,[142–147] which was achieved by the interaction of the methane-sulphonate (LXX)[102] with the potassium thiolate derived from the methyl ester of *N*-trifluoroacetyl-L-cysteinylglycine (LXI):[142]

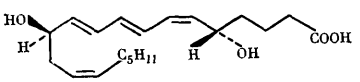


(LXX) 5-deoxy-$LTD_4$

All the diastereoisomers of 5-deoxy-$LTD_4$ synthesised exhibited only 1% of the activity of the natural $LTD_4$, which indicates the importance of the hydroxy-group at C(5) for the manifestation of the biological activity of $LTD_4$.

### 3. The Synthesis of Leukotriene $B_4$ and its Isomers and Analogues

Leukotriene $B_4$, namely 5(*S*),12(*R*)-dihydroxy-6*Z*, 8*E*, 10*E*, 14*Z*-eicosatetraenoic acid, is a chemotactic and chemokinetic† factor, which plays an important role in inflammatory processes and is a metabolite of arachidonic acid in its lipoxygenase oxidation, namely in the stage involving the enzymic hydrolysis of $LTA_4$ (Scheme 3).



$LTB_4$ (II)

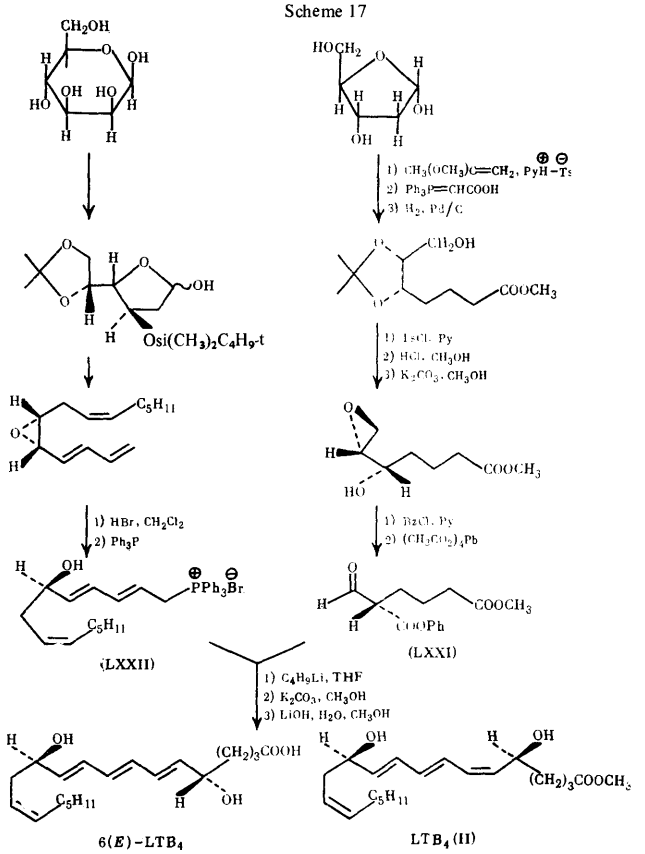
The synthesis of $LTB_4$ is based on the same principles as the synthesis of $LTA_4$, but the characteristic features of the structure, namely the presence of hydroxy-groups at C(5) and C(12) in the hydrocarbon chain, introduced definite differences into the construction of the $LTB_4$ molecule. The synthesis is carried out by the Wittig condensation of two fragments—the hydrocarbon fragment [up to C(20)] and the carboxyl-containing fragment [from C(1)].[51,148–169] The aldehyde functional group, which is essential for the Wittig reaction, is located in the carboxy-fragment, while the hydrocarbon component is constructed in such a way that, before the Wittig condensation, it contains either the hydroxy-group at the C(12) carbon atom or groups which are readily converted to such a hydroxy-group, as well as three double bonds.

---

†Chemotaxis is the motor response of freely migrating cells of multicellular organisms under the influence of a unilateral chemical irritant.

The synthesis of natural $LTB_4$ was first proposed by Corey and was important in the determination of the structure of this compound[51,114,148] (Scheme 17). The chiral aldehyde (LXXI), the C(1)–C(6) fragment of the $LTB_4$ molecule, was obtained from 2-deoxyribose in several stages. The phosphonium salt (LXXII) [the C(7)–C(20) fragment] was synthesised from D(+)-mannose, as described previously.[114] The Wittig reaction of compound (LXXI) and (LXXII) followed by hydrolysis afforded $LTB_4$ with an admixture of 6*E*-$LTB_4$. The synthetic $LTB_4$ specimen is identical with the natural product and has the 6*Z*, 8*E*, 10*E*, 14*Z*-configuration of the double bonds.

Scheme 17




In order to confirm the structure of the natural $LTB_4$,[148–153] its 6*E*, 8*Z*- and 6*E*, 10*Z*-isomers, which possess no biological activity, were synthesised.[149] For this purpose, the stereospecific syntheses of the biologically active 5(*S*),12(*S*)-stereoisomer of 6*E*, 8*Z*-$LTB_4$,[143,149–152] and the 5(*S*),12(*R*)- and 5(*S*),12(*S*)-stereoisomers of 6*E*-$LTB_4$ [152–158] were carried out.

After the determination of the structure, more convenient methods of synthesising the natural $LTB_4$ were sought. A synthesis of $LTB_4$ from the epoxyphosphonium salt (LXIII) [97,106,149] and the aldehydoester (LXXI) [122] in accordance with Scheme 18 has been proposed.[150]

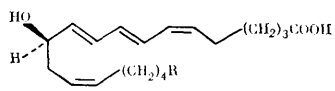
A stereospecific synthesis of $LTB_4$ from 2-deoxy-D-ribose, used previously by the same workers in the synthesis of series 4 leukotrienes ranging from $LTA_4$ to $LTF_4$ and their isomers,[155] was proposed in 1982.[154]

In another synthesis of $LTB_4$ and its 12(*S*)-epimer (IIa) (Scheme 20), the authors[156] used L- and D-arabinose respectively as the initial compounds to generate the chiral centre at C(12). L-Arabinose is converted by a standard method[157,158] in six stages to the aldehyde (LXXIV), which is then transformed by means of a series of reactions into $LTB_4$. The 12(*S*)-isomer of $LTB_4$ was obtained analogously from D-arabinose.

Enantiomeric epoxidation[127,128] greatly simplified the synthesis of the natural $LTB_4$.[159]

In 1983 it was suggested[160] that the optically active aldehydes (LXXI) [148,151,152,154] and (LXXV) [156] be synthesised from cinnamaldehyde rather than from carbohydrates.

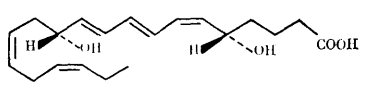
Two $LTB_4$ metabolites have been isolated and identified comparatively recently: ω-carboxy-$LTB_4$ (LXXVIa) [161–167] and ω-hydroxy-$LTB_4$ (LXXVIb),[161–167] which were synthesised[163] via a scheme developed previously:[154–156]



(LXXVI)

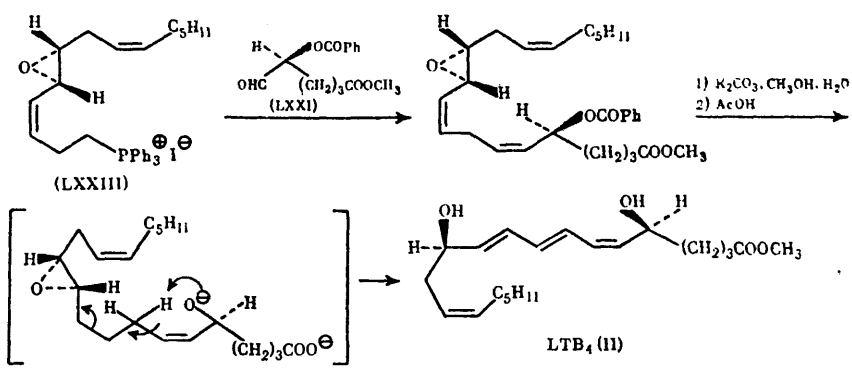
R = COOH; $CH_2OH$

$LTB_5$ (LXXVII), previously obtained by biosynthesis,[169] was synthesised in 1983:[168]

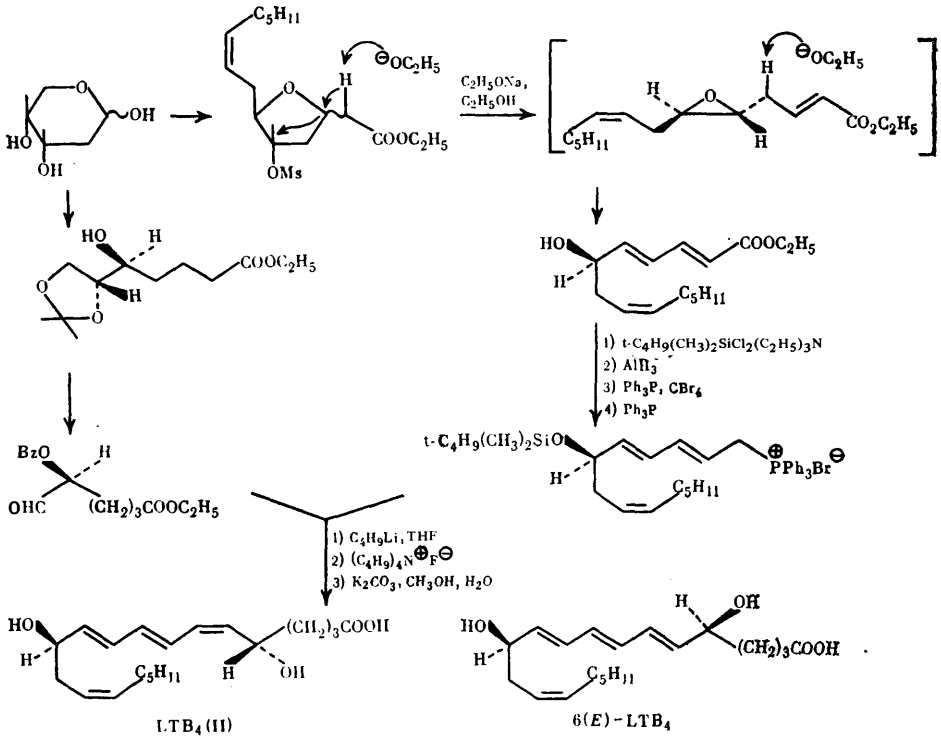


$LTB_5$ (LXXVII)

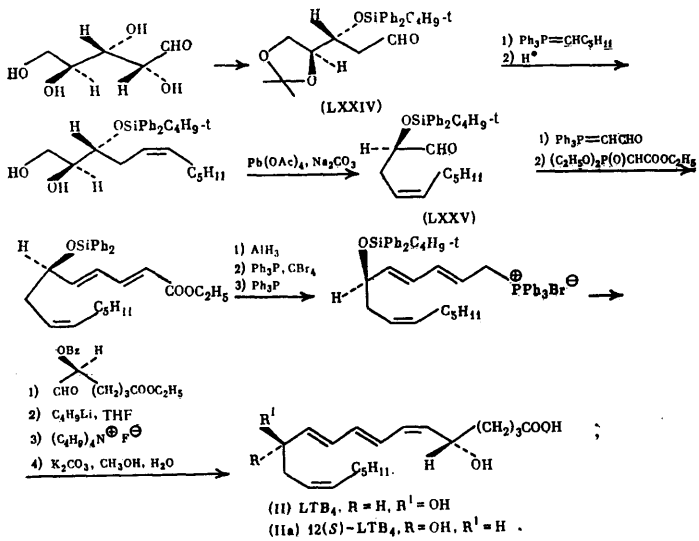
Scheme 18



Scheme 19




Scheme 20



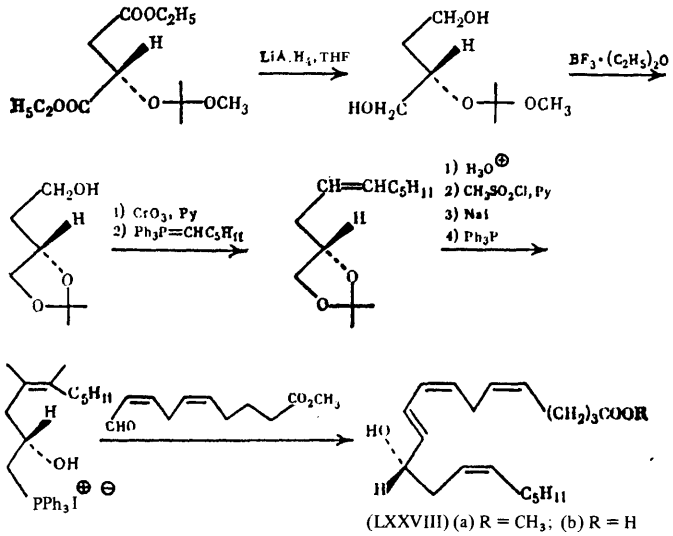

## IV. THE SYNTHESES OF OTHER OXYGEN-CONTAINING ACYCLIC ARACHIDONIC ACID METABOLITES

The initial compounds arising in the enzymic oxidation of arachidonic acids are the hydroperoxyeicosatetraenoic acids (VI) and the hydroxyeicosatetraenoic acids (XIII), which were designated in the literature by the abbreviations 5-TPETE and 5-HETE# [8,137,170–180] (Scheme 3) respectively. These biologically active compounds have been discovered in the human and animal organisms. Extremely little is known about the biological role of HETE in cell functions or about their biological precursors (HPETE). However, the fact that their formation from arachidonic acid is not inhibited by aspirin and indomethacin, in contrast to the prostaglandin endoperoxides ($PGG_2$ and $PGH_2$), and their high content in certain tissues (for example, human epidermic tissues in persons suffering from the skin disease psoriasis) makes them extremely interesting for comprehensive study.[8,176]

#Apart from 5-HETE, 11-, 12-, and 15-HETE are known for arachidonic acid,[8,171–175] and their corresponding HPETE precursors.[8,171]

The total synthesis of 12(*S*)-hydroxy-5*Z*, 8*Z*, 14*Z*, 10*E*-eocosatetraenoic acid (LXXVIIIb), which has been called "Samuelsson's HETE" was first achieved in 1978 [104] in accordance with Scheme 21:

Scheme 21



(LXXVIII) (a) R = $CH_3$; (b) R = H

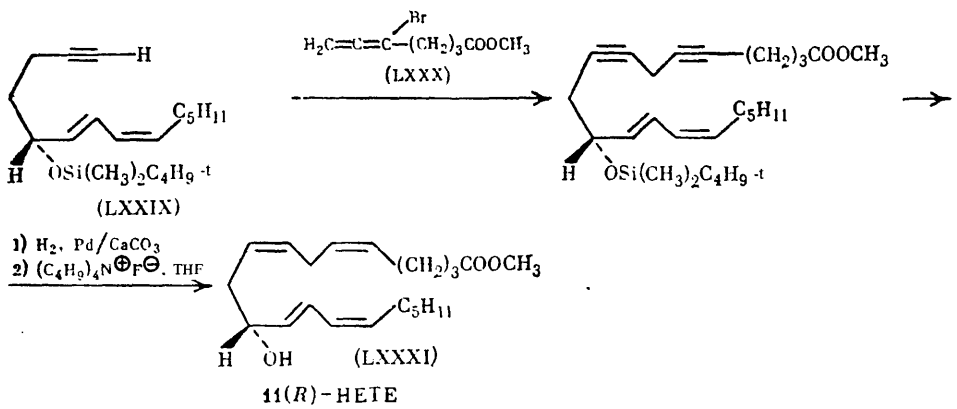
The oxidation of arachidonic acid by oxygen[177,178] leads as a rule to a random mixture of HPETE and HETE which is extremely difficult to use for comparative purposes.[179] However, it has been suggested[54] that (±)-5-HETE and (±)-5-HPETE be synthesised by selective substitution at the C(5) atom in the arachidonic acid molecule. (±)-5-HETE has been prepared by other investigators[181] in accordance with an analogous idea involving the introduction of the phenylseleno-group into arachidonic acid.

The (*S*)-enantiomer of 5-HETE discovered in natural sources, which is an important biological mediator functioning as a chemotactic agent for human leukocytes (eosinophils and neutrophils), and its (*R*)-enantiomer have been obtained by the chromatographic separation of the diastereoisomeric urethanes.[54,182] 5-(*S*)-HETE (VI) is a stronger chemotactic factor than 8-, 9-, 11-, 12-, and 15-HETE and its importance is comparable to that of the peptide derivatives involving the C(5) carbon atom.[182]

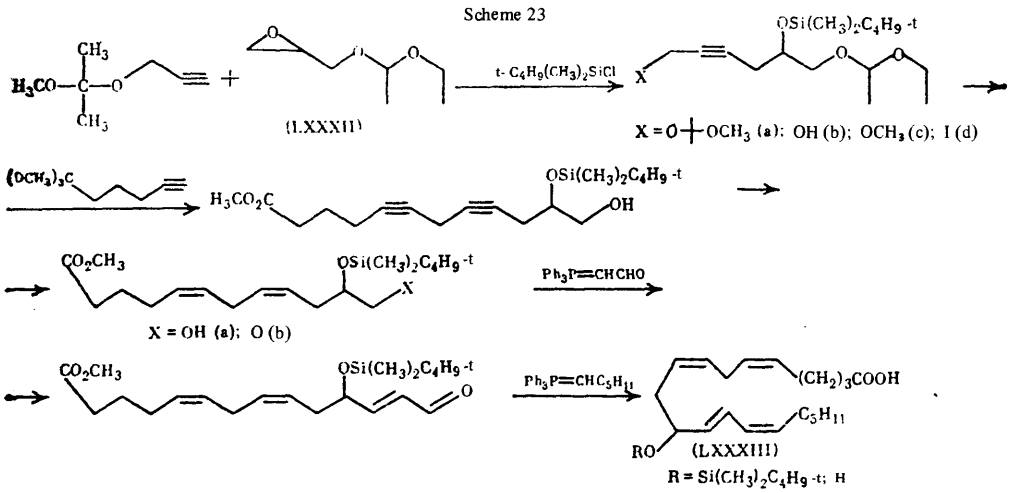
The synthesis of 5(*S*)-HETE (VIa) and 5(*R*)-HETE (VIb) via a scheme developed using the Wittig reaction[106,154,184] has been published.[183]

The methyl ester of 11(*R*)-HETE (LXXXI) has been synthesised[185] by a novel reaction of allene bromide (LXXX) with silyl derivatives of a terminal acetylenic diene (LXXIX) (Scheme 22). The same workers[171] achieved the synthesis of 11-, 12-, and 15-HETE from 11,12- and 14,15-epoxyarachidonic acids.

Scheme 22



Scheme 23



An alternative synthesis of 11(*R*,*S*)-HETE (LXXXIII) has been achieved[186] using the glycidol derivatives (LXXXII) (Scheme 23).

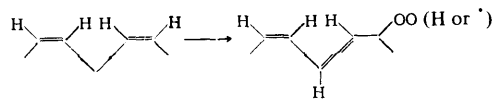
The 11(*R*)- and 11(*S*)-isomers of HETE have been synthesised by a new method involving the resolution of the initial mixture of diastereoisomeric acetoxyaldehydes with the aid of ephedrine.[187]

The syntheses of HPETE, which are precursors of HETE, have been described in a number of studies.[97,102,182]

## V. THE SYNTHESES OF INHIBITORS OF THE ENZYMIC OXIDATION OF ARACHIDONIC ACID

Four oxidative pathways leading to the biosynthesis of biologically active eicosanoids from arachidonic acid under the influence of lipoxygenase are known.[188] Among them the pathway leading to the formation of leukotrienes [the 5-lipoxygenase (5-LO) pathway] is of special interest.[188,189] The biosynthesis of prostaglandins (PG) and thromboxanes (TX) via the lipoxygenase reaction of arachidonic acid involving C(11), catalysed by the enzyme cyclo-oxygenase (CO), has been studied to a considerable extent.[190]

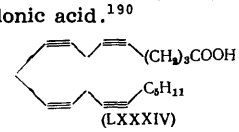
Both pathways involve the initial oxidation of the lipoxygenase type in which the 1*Z*, 4*Z*-pentadiene unit (A) is converted into the 1-oxygenated 2*E*, 4*Z*-pentadiene fragment (B):[171,188,191,192]




(A) (B)

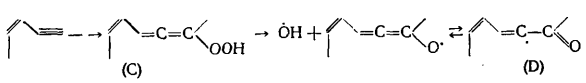
Studies using various lipoxygenase, namely 5-LO from mammalian leukocytes,[8,180,192] potato tubers,[8,180,192] and other sources,[8] 12-LO from thrombocytes,[192] 15-LO from soya beans,[8,171,189,193] and others,[8] justify the hypothesis that the transformation A → B may be specific to the lipoxygenase catalysis.[192,194,195]

It has been found that aspirin, indomethacin, and a number of other non-steroid anti-inflammatory agents inhibit the biosynthesis of prostaglandins by blocking the initial stage of the lipoxygenase reaction of arachidonic acid at C(11), catalysed by cyclo-oxygenase.[8,189–191,196] The mechanism of the action of these empirically discovered and therapeutically important inhibitors of the prostaglandin biosynthesis is obscure but it has been demonstrated convincingly that they block the action of 11-LO but are ineffective as inhibitors of other biological oxidation pathways, including the 5-LO pathway.[189–191] 5,8,11,14-Eicosatetraynoic acid (LXXXIV), which has been synthesised by the author of this review,[197,198] inhibits the 11-, 12-, and 5-lipoxygenase reactions of arachidonic acid.[190]



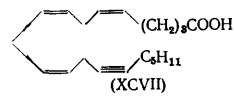

(LXXXIV)

It has been suggested[189,199] that monodehydroarachidonic acid should bind more strongly and more selectively to lipoxygenase, preventing the oxidation of natural arachidonic acid. The lipoxygenation of the acetylenic linkage gives rise to the olefinic hydroperoxide (C) and the dissociation of the O–O bond leads to the formation of the radicals OH• and (D),[189] which evidently results in the deactivation of lipoxygenase:




(C) (D)

To confirm this hypothesis, Corey and Kang[199] synthesised 5,6-, 8,9-, and 11,12-dehydroarachidonic acids (DHA) [compounds (LXXXV), (LXXXVI), and (LXXXVII) respectively] and investigated them in lipoxygenase oxidation processes.[188,189] A fundamentally new method for the formation of the C–C bond in the construction of the *Z*-RCH=CHCH$_2$C≡R structure by the reaction of the iodo-olefins (LXXXIXb), (XCI), (XCII), and (XCb), obtained from the butylstannanes (LXXXVIII),[199,200] (LXXXIXa),[201] and (XCa),[201] with the iodoallenes (XCIII) and (XCIV),[185] (XCV),[202] and (XCVI) respectively, has been proposed in the syntheses of DHA (Scheme 24).[199] The synthesised DHA specimens were identical with those synthesised previously[122,188] using acetylenic compounds and the Wittig reaction.



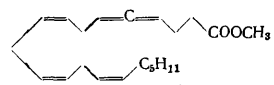

(XCVII)

Like 5,8,11,14-eicosatetraynoic acid, 5,6-dehydroarachidonic acid was synthesised by the authors of this review[197,203] from acetylenic derivatives by nucleophilic substitution at the terminal acetylenic carbon atom—a method proposed by Osbond and Wickens[204] and subsequently modified and improved by other workers.[205,206]

14,15-Dehydroarachidonic acid (14,15-DHA) (XCVII) was synthesised by arachidonic acid via the opening of the epoxy-ring[131] and the formation of a triple bond via a reaction involving ketobromides.[189]

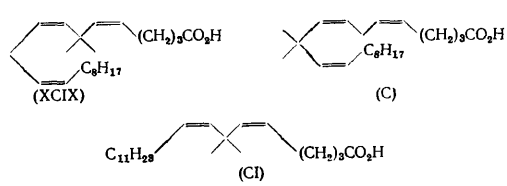
It has been shown[188,189,190] that 4,6-DHA and 14,15-DHA inhibit irreversibly only soya bean 5-LO and 15-LO respectively. A most effective inhibitor of the biosynthesis of prostaglandins is 11,12-DHA. 14,15-DHA can inhibit the formation of prostaglandins but at much higher concentrations than 11,12-DHA. 5,6-DHA and 8,9-DHA are not only inhibitors of the biosynthesis of prostaglandins but at higher concentrations can actually behave as substrates.

4,5-Dehydroarachidonic acid (4,5-DHA) (XCVIII), which is an irreversible and more selective inhibitor of the 5-LO from basophilic leukaemic rat cells,[207–209] the mechanism of the action of which on the enzyme is apparently different from that of 5,6-DHA, has been synthesised from 5,6-epoxyarachidonate (LIX).[131]




(XCVIII)

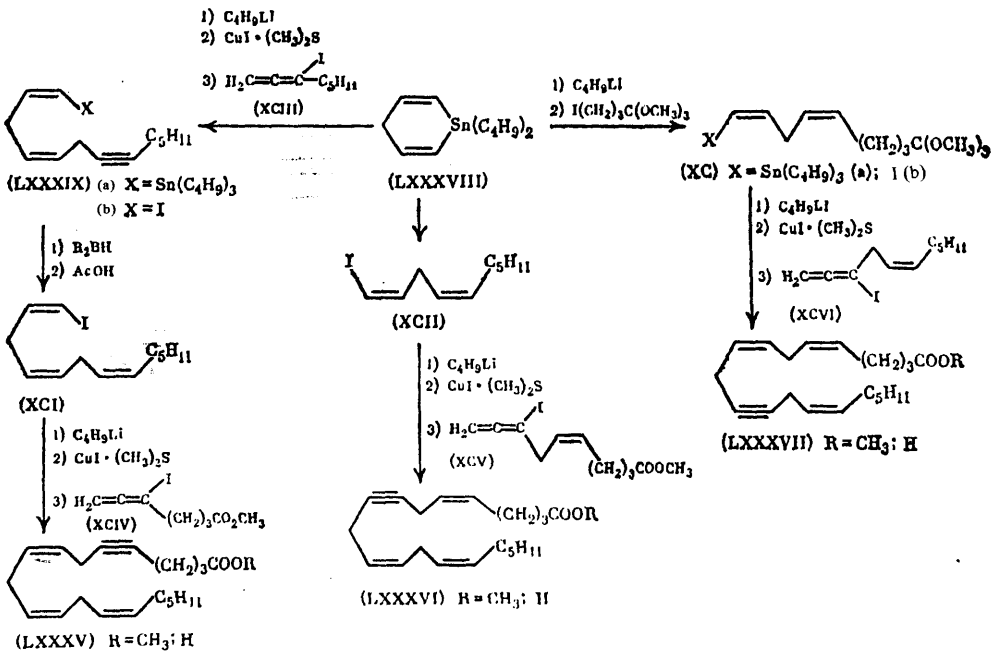
5-LO is inhibited by 7,7- and 10,10-dimethyl-5*Z*, 8*Z*, 11*Z*-eicosatrienoic acids (XCIX) and (C),[176] and also by 7,7-dimethyl-5*Z*, 8*Z*-eicosadienoic acid (CI),[191] which are derivatives of 5,8,11-eicosatrienoic acid—the substrate in the biosynthesis of series 3 luekotrienes.[8,41,122] The inhibitors (XCIX), (C), and (CI) have been synthesised from acetylenic compounds by means of the Wittig reaction.[176]



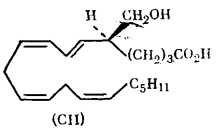

(XCIX) (C) (CI)

5,6-Methanolaukotriene $A_4$, the "carbo-analogue of $LTA_4$", (XLIXa),[117,118,210] the thio-analogue of $LTA_4$ (XLIXb),[122] and 5-hydroxymethyleicosatetraenoic acid (CII),[118] which are synthetic analogues of the selective inhibitors of the

Scheme 24



biosynthesis of leukotrienes, possess the properties of the latter.



(CII)

## VI. THE BIOLOGICAL ROLES UF LEUKOTRIENES

The leukotrienes $C_4$, $D_4$, $F_4$, and $B_4$ are of considerable interest as a new class of natural physiologically active bioregulators.[6,8,59,111,138,144,192,210–222] Leukotrienes have been identified both in leukocytes and in a series of other sources, which indicates their wide distribution.[6,8,144,211,212]

Purified SRS-A, isolated from natural sources, and the synthetic $LTC_4$, $LTD_4$, and $LTE_4$ are as a rule tested for their ability to contract the smooth muscle tissue in guinea-pig intestines in the presence of histamine antagonists.[8] The studies of the action of leukotrienes on the guinea-pig aorta,[118] bronchi,[99] and trachaea[92] and human bronchi *in vitro*[8,211,212] have shown that $LTC_4$ and $LTD_4$ increase microvascular permeability and are powerful spasmogenic agents in relation to bronchi, acting on the smooth muscle tissue in peripheral air pathways.[8,94,96,183,212] $LTC_4$ and $LTD_4$ make the main contribution to the biological activity of SRS-A.[192] The leukotriene $F_4$ is 282 times less active than $LTD_4$.[143] $LTD_4$ contributes more than 90% of the biological hypersensitivity of human lungs. Leukotriene $D_4$ is 1000 times more active than $LTC_4$.[143,213] Since leukotrienes are secreted in the course of immunological action, it is extremely probable that cells serving as receptors of immunoglobulins E (or G in guinea-pigs) serve as sources of leukotrienes.[6] It has been suggested that SRS is liberated together with other mediators (histamine and chemotactic factors).[6,8]

The study of the action of $LTD_4$ as a function of concentration in the presence and absence of selective inhibitors of the biosynthesis of leukotrienes[8] has confirmed the existence of two separate receptors in peripheral airways. The study of the effects of $LTC_4$ and $LTD_4$ on pulmonary mechanics and the arterial blood pressure[93,213] has shown that both leukotrienes can contract human bronchi[23,214] (1000 times more actively than histamine)[8,213] and has confirmed the fact that $LTC_4$ and $LTD_4$ act as mediators in the bronchial spasm in bronchial asthma[93,138] and other instant hypersensitive responses.[211] The discovery of the biological activity of $LTC_4$ and $LTD_4$, which is comparable to the activity of histamine, explained why the attempts to alleviate the symptoms of bronchial asthma by antihistamine preparations were unsuccessful.[8] The fact that their precursor, arachidonic acid, can be converted into both prostaglandins and leukotrienes, explained the unfavourable effect of non-steroid anti-inflammatory agents on asthmatic symptoms in aspirin-sensitive patients.[211,212] Thus the arachidonic acid balance, disturbed by cyclo-oxygenase inhibitors, increases the concentration of leukotrienes with a corresponding increase of the intensity of the bronchial spasm. It has been possible to account for the successful treatment with corticosteroids in asthma therapy. These substances block the action of phospholipase $A_2$, which is involved in the cleavage of phospholipids and the secretion of arachidonic acid, which ultimately reduces the degree of biosynthesis of leukotrienes.[8] Studies on the possibility of the contraction of smooth muscles by a series of $LTC_4$ and $LTD_4$ analogues made it possible to formulate a structural requirement which must be met by compounds in order that they can manifest such biological activity.[8] Positional isomers with peptide substituents at sites other than C(6) exhibit a weak ability to contract smooth muscles.[23,93,94,102,104,146,213,214] It has been shown that the 5(*S*),6(*R*)-configuration of the substituents must be maintained.[102,215] Diastereoisomers are less active by two orders of magnitude. The fully saturated analogues of $LTC_4$, $LTD_4$, and $LTE_4$ are in essence inactive.[140] The change in the geometry of the

double bond from 11*Z* to 11*E* results in a significant loss of activity.[75,212] The biological activity of the 7-*cis*-isomer of $LTD_4$ amounts to only 1/10 of the activity of the natural $LTC_4$.[99] The results obtained in the study of 38 analogues of leukotrienes have shown[146,147] that their hydrophobic component and their stereochemical features influence the manifestation of their activity. Analogues lacking the natural structure of the hydrophobic component of the leukotriene molecule are much less active. The terminal amino-group in the peptide side chain, the carboxy-group of glycine, and the C(5)-hydroxy-group[114] are extremely important for the manifestation of the maximum biological activity. On the other hand, the carboxy-group at C(1) is not an important component. Changes in the aminoacid residue present in $LTD_4$ entail some loss of biological activity. These results have led to the conclusion that the receptor for $LTD_4$ as regards its binding and the generation of the response[114] must consist of a broad hydrophobic binding site, adjoining a multicomponent active section, which should bind the non-ionised C(1)-carboxy-group, the C(5)-hydroxy-group, and the peptide functional group containing a non-protonated amino-group.[114]

Leukotriene $B_4$ induces the contraction of various preparations of the smooth muscle of the guinea-pig.[8,144,211-216] The duodenum is the organ most sensitive to the action of $LTB_4$, but the greater stability of the parenchymal§ component of the lung renders this tissue more suitable for biological tests. Leukotriene $B_4$ is closely associated with inflammatory processes and behaves as a chemotactic[146,154,156] and chemokinetic factor for neutrophil and eosinophil, which arise in large amounts (at a concentration of $3 \times 10^{-9}$ M) in inflammatory states.[162-166,212] This activity is greater by 2–3 orders of magnitude than the activity of mono-HETE. An increase of the content of $LTB_4$ has been observed in the synovial fluid of patients suffering from inflammatory diseases.[212,217] In combination with vasodilators of the type of $PGE_2$, leukotriene $B_4$ increases vascular permeability.[212,218] Prostaglandins synergise this effect, increasing the blood flow.[165,211,212] The release of lysozyme by the products of the metabolism of arachidonic acid[211,212,219] and apparently $LTB_4$ has been described. Even low concentrations of hydroxyeicosatetraenoic acids increase the content of cyclic guanosine monophosphate (c-GMP),[220] which is believed to promote, in its turn, the release of lysozyme[211] in phagocytotic processes. A change in the geometry of the double bonds of the conjugated triene[51,149,153] and of the configuration of the C(12)-hydroxy-group[156] in the natural structure lead to an appreciable decrease of the biological activity of $LTB_4$.[154,156] The unique lipoprotein nature of leukotrienes and their close relation with a whole series of pathological states underlying many diseases[8,211,212] [bronchial asthma, Quincke's (angioneurotic) oedema, vasomotor rhinitis, rheumatoid arthritis, psoriasis, etc.] and their role as long-acting regulators of nerve excitability by allergic reactions[211,212] have given rise to the question how molecules of these compounds function in the organism and how they are deactivated biochemically.[144] The answers to these questions can apparently be provided by a detailed study of the biological role of leukotrienes. Analogues and antogonists of leukotrienes, the inhibitors of their biosynthesis, the synthesis and study of the properties of which accelerate the search for effective antiallergic preparations, are of great interest for this purpose.

§ Parenchyma consists of a set of cellular elements of the organ which effects its specific functions. It can be made up of various types of tissue: blood generating tissue (spleen), epithelium (glands), nerve cells (nerve ganglia), etc.

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# Characteristic Features of the Chemical Properties of Fluorine-containing Unsaturated Compounds†

N.P.Gambaryan and E.M.Rokhlin

The review deals with the results obtained in the study of the chemical properties of organofluorine and saturated compounds containing the C = C, C = O, C = N, C = C = C, C = C = O, C = C = N, etc. groups. The characteristics of the reactions of fluoro-olefins and related compounds with nucleophiles as well as the methods of synthesis and the properties of fluorocarbanions (including mesomeric fluorocarbanions) are examined. The electronically amphoteric character of the C = C bond in fluorine-containing unsaturated compounds, ensuring the possibility of interaction with strong electrophiles, and the synthetic possibilities resulting from these reactions are demonstrated. The analogy between the chemical properties of polyfluoro-substituted carbonyl compounds, their derivatives, heterocumulenes, and nitro- and nitroso-compounds is discussed. The influence of fluorine atoms is manifested by the markedly electrophilic properties of these compounds and in many cases also by the singular stability of the unusual structures formed as a result of their reactions.
The bibliography includes 180 references.

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## I. INTRODUCTION

The establishment of the organic chemistry of fluorine as a separate branch of science dates back to the beginning and middle 1940's.[2] The development of this field was initially dictated by immediate practical needs (the necessity for the creation of materials resistant to the action of uranium hexafluoride). Since then organofluorine compounds are being increasingly used in a wide variety of fields, so that "it is at present difficult to name a branch of engineering which could do without materials containing fluorine".[2]

The possibilities in the application of fluorine compounds are determined by the characteristic features of this element. Fluorine is the most electronegative element in the Periodic System. The dissociation energy of its molecules is extremely low (the same as that for iodine) and the strength of its bonds with many elements is, on the other hand, high. As a result of this, the majority of substances, even the inert gases, can interact with fluorine.

Perfluorocarbon chains are exceptionally stable both thermally and chemically owing to the great strength of the carbon–fluorine bond (on average about 110 kcal $mol^{-1}$) and also the very favourable ratio of the carbon–carbon bond length to the size of the fluorine atom. The van der Waals radius of fluorine is smaller than the C–C bond length and for this reason the accumulation of fluorine atoms in perfluorocarbons does not lead to the extension and weakening of this bond (as in perchlorocarbons); on the contrary, fluorine atoms give rise to close packing, reliably protecting the carbon chain from external influences and in particular rendering it resistant to oxidation.

All these factors led to an abundance of compounds of a wide variety of classes in which all the hydrogen atoms have been replaced by fluorine. Organofluorine chemistry, which is, as it were, a copy of organic chemistry, has been created. However, this copy is so unusual and the results have so far been so unexpected that they have enriched organic chemistry and have greatly extended its theoretical ideas.

Since the creation of the Institute of Organoelemental Compounds of the USSR Academy of Sciences (INEOS) in 1954, the Laboratory of Organofluorine Compounds, headed by Ivan Lyudvigovich Knunyants, was organised in it. In the present review an attempt is made to survey some of the most interesting and important results obtained by the members of this laboratory during the one-third of a century of its existence. Many of these results have been described in a series of other reviews.[2–26] In describing the relevant data, we shall as a rule refer to these reviews and the original papers will be quoted only in the case of the latest investigations.

The principal direction taken by the studies in the above laboratory involves the investigation of the characteristic features of various multiple bonds in organofluorine compounds such as fluoro-olefins, including those with functional group substituents (the C=C bond), carbonyl compounds and their derivatives (the C=O, C=N, etc. bonds), nitro- and nitroso-compounds (the $N\overset{O}{\underset{O}{<}}$ and N=O groups), and cumulenes and heterocumulenes (the C=C=C, C=C=O, C=C=N, N=C=O, etc. groups). The present review is mainly devoted to these studies.

However, apart from the investigations of the multiple bonds, other branches of organofluorine chemistry also occupy an important place in the studies carried out in the Laboratory. Frequently these investigations are genetically related to the main field of study. Thus, numerous reactions of fluorine-containing unsaturated compounds, leading to the formation of carbocyclic and heterocyclic systems, including those with small rings, have been discovered. The study of the properties of these cyclic systems, which are frequently unusual, is of considerable interest.[2,3,13,16,27–31]

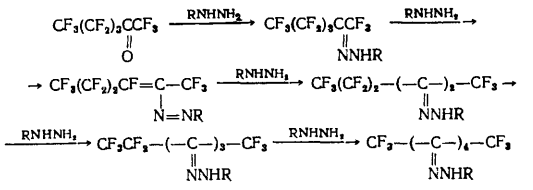
Fluorocarbanions, which are of very great synthetic importance# (see below), are formed as intermediates in various reactions of fluoro-olefins and related compounds in the presence of the $F^-$ anion.

†The article has been written to commemorate the 80th birthday of the founder of the Soviet school of organofluorine chemists Academician I.L.Knunyants (cf.Rokhlin and Gambaryan[1]).

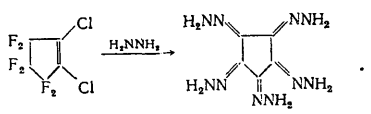
#Another important property of the $F^-$ anion, namely its high basicity, was discovered by Knunyants and co-workers as early as the middle 1940's;[32] this property is nowadays used widely for synthetic purposes.[2,33–35]

The study of the reactivities of fluoroketones yielded functional-group derivatives of 2,2-diphenylhexafluoropropane and aryl- or alkyl-bis(fluoroalkyl) carbinols. Compounds of these types have been the objects of two major series of investigations associated with the development of methods of synthesis of monomers for polycondensation polymers with valuable properties,[36,37] and fluorine-containing epoxides—intermediates in many syntheses of organofluorine substances.[2]

Knunyants introduced the bold idea of an analogy between the $CF_2$ and C=O groups,[5] which proved fruitful as regards syntheses. In particular, a rearrangement of fluoroalkyl azides, resembling the Curtius rearrangement of acyl azides, was discovered.[5] Like keten, a terminal fluoro-olefin is capable of undergoing reactions of the Wittig–Staudinger type.[13] Perfluoromonocarbonyl compounds behave similarly to polycarbonyl compounds, forming osazones and polyhydrazones,[38,39] for example:

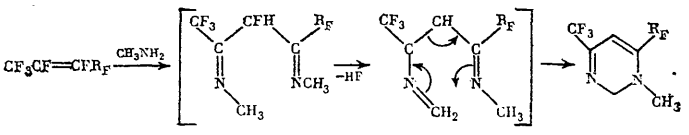


In the series of alicyclic compounds it has actually been possible to obtain "perhydrazones",[39,40] for example:

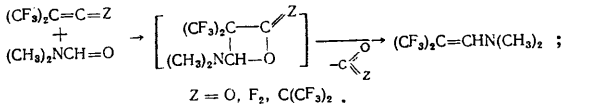


These interesting reactions demonstrate the possibility of "livening" the perfluorocarbon chain. They are based on the ability of hydrazones of α-fluoro-substituted carbonyl compounds to be dehydrofluorinated with formation of unsaturated azo-compounds which then react with the next mole of hydrazine.

Such dehydrofluorination is apparently possible also for α-fluoroketone methylimines. This explains the unexpected result of the interaction of certain internal perfluoro-olefins with methylamine, which leads to dihydropyrimidines.[41] The intermediate heptafluoroacetylacetone diimine (cf. Kurykin et al.[42]) is dehydrofluorinated to a 1,3,5-heterotriene, which is converted into a substituted dihydropyrimidine as a result of intramolecular [4 + 2]-cycloaddition:



An analogy has also been observed in the reactions of fluorine-containing unsaturated compounds with dimethylformamide, leading to the products of the cleavage of the unstable oxetans formed initially. Bis(trifluoromethyl)keten,[20] perfluoroisobutene,[22] and perfluorotetramethylallene[43] give rise to hexafluoroisobutenyldimethylamine under these conditions:



Z = O, $F_2$, $C(CF_3)_2$ .

In the latter case the hexafluoroisobutenylidene group $C=C(CF_3)_2$ acts as an analogue of the carbonyl group.

Much attention has been devoted to the methods for the introduction of fluorine into an organic molecule. In particular, this applies to the discovery of the opening of the epoxide rings under the influence of HF, first discovered by Knunyants and co-workers,[32]§ and the coupled addition to olefins in hydrogen fluoride.[19] A number of studies have been devoted to the fluorination of organic compounds.[46–48] A convenient synthesis of the anticancer preparation 5-fluorouracil by the direct fluorination of the readily available uracil has been developed and introduced into practise.[46]

A method for the partial introduction of fluorine into organic molecules under mild conditions by means of anodic oxidation in the presence of the fluoride anion at low potentials is of special interest.[14,23] The method for the electrochemical trifluoromethylation of organic compounds (for example, of olefins, derivatives of αβ-unsaturated carboxylic acids, and aromatic compounds) with the aid of the $CF_3$ radical generated in the anodic oxidation of trifluoroacetic acid is also interesting.[49]

Studies on the synthesis and properties of chemically inert organic perfluoro-compounds, with an anomalously high capacity for dissolving various gases, in particular $O_2$ and $CO_2$, are very important. Such compounds are attracting increasing attention because various preparations for biomedical purposes, including artificial blood substitutes, can be obtained on their basis.[50]

However, as already stated, the principal research carried out at the Laboratory was devoted to the investigation of the reactions of multiple bonds in organofluorine compounds, particular emphasis being laid on the study of the C=C bond.

## II. FLUORO-OLEFINS AND RELATED COMPOUNDS

The comparatively readily available fluoro-olefins can be regarded as "key" compounds in the organic chemistry of fluorine. An enormous range of the most varied organofluorine compounds can be obtained from them; in addition, the study of the reactivity of fluoro-olefins and related compounds made it possible to elucidate many important theoretical questions relevant to organofluorine chemistry (and organic chemistry in general).

The unusual chemical properties of perfluoro-olefins are caused by the high electronegativity of the fluorine atom and the ability of its electrons to effect various types of conjugation in the molecule. In contrast to the usual hydrogen-containing olefins, perfluoro-olefins react very readily with nucleophiles.[45,51]

Soon after the first communications on the addition of nucleophiles to fluoroethylenes,[52,53] the studies by Knunyants and co-workers, devoted to the interaction of various fluoro-olefins with nucleophiles, were published.[54–56] Perfluoroisobutene proved to be especially active in these reactions. Studies of its chemical properties, which have continued to this day, demonstrated the truly inexhaustible synthetic possibilities arising from the use of this fluoro-olefin.[22] Other branched perfluoro-olefins, in particular perfluoropropene dimers and trimers, for example, $(CF_3)_2C = CFC_2F_5$ and $CF_3CF = C[CF(CF_3)_2]_2$,[57–67] have attracted much attention recently. Their interaction with nucleophiles lead to ways of synthesising potential monomers, fluorine-containing surfactants, and other products of practical value.

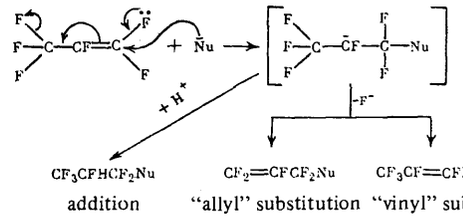
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§ This reaction has found extensive applications, for example, in the synthesis of fluorine-containing steroids.[44,45]

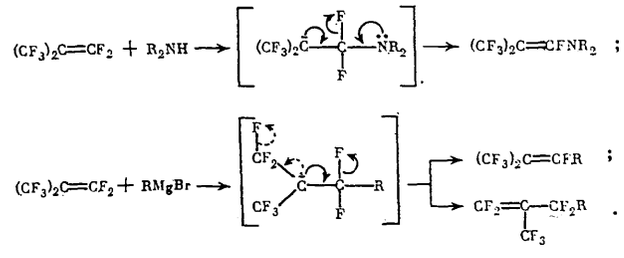
In the study of the reactivity of the C=C bond "depleted" in electrons owing to the influence of the fluorine atoms and the perfluoroalkyl groups, a wide range of other fluorine-containing compounds with a C=C bond were also investigated, namely, 1,3-dienes,[6,68–71] allenes,[2,43,72–74] derivatives of αβ-unsaturated carboxylic[5,11,24,75–79] and phosphonic[78,80] acids, and alkyl polyfluoroalkenyl ethers.[6,7,60,63,81–83] The most varied nucleophiles, including unusual ones, have been involved in reactions which yielded interesting and sometimes unexpected results.

The first investigations already revealed the occurrence of "vinyl" substitution in perfluoropropene and perfluoroisobutene.[56] This reaction was surprising from the standpoint of the "usual" organic chemistry, but it was found to be common in the chemistry of organofluorine compounds.

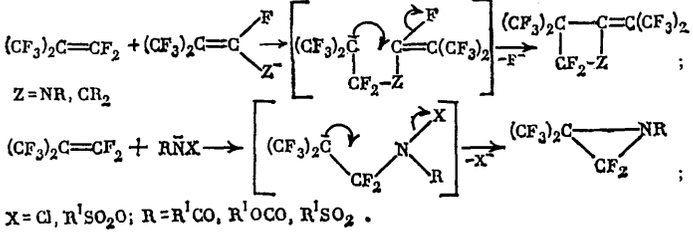
Subsequently it was shown (to a large extent as a result of the work of Knunyants and his school) that, in the reactions of fluoro-olefins with nucleophiles, the direction of attack depends on the conjugation in the fluoro-olefin molecule and the final result depends on the realisation of various possibilities for the stabilisation of the intermediate carbanions:[2,3,22,51]




These possibilities are determined both by the structure of the initial fluoro-olefin and by the nature of the nucleophile. In particular, the contribution of the "allyl" substitution increases in the absence of an unshared electron pair in the substituent obtained from the nucleophile:[22]



Instances of the stabilisation of the intermediate carbanions by intramolecular cyclisation are of special interest,[13,22,60,77,84–87] for example:



The anions $RCO\bar{N}X$, formed in the Hofmann and Lossen rearrangements, were "captured" with the aid of a reaction of this type for the first time.[22]

The intense electron-accepting effect of the trifluoromethyl groups in perfluoroisobutene and related compounds leads to the possibility of obtaining geminal compounds as a result of "double vinyl substitution",[22,56,88,89] for example:

$$(CF_3)_2C{=}CF_2 \xrightarrow{R_2NH} (CF_3)_2C{=}C(NR_2)_2 .$$

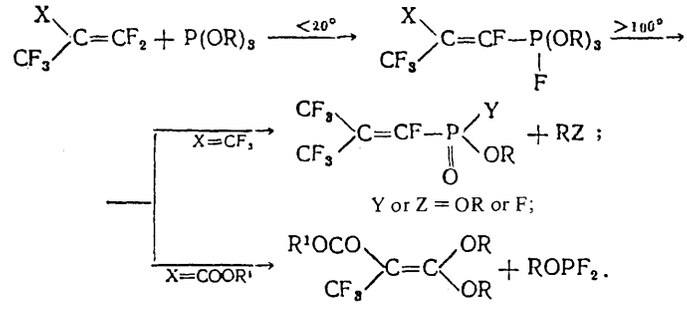
Novel methods of synthesising fluorine-containing cumulenes and heterocumulenes are also based on the substitution of both fluorine atoms in the $=CF_2$ group,[13,22,77,90] for example:

$$(CF_3)_2C{=}CF_2 + H_2NR \xrightarrow[-(CF_3)_3CH]{(CF_3)_2C=CF_2} (CF_3)_2C{=}C{=}NR ;$$

$$(CF_3)_2C{=}CF_2 + CH_2(COOR)_2 \xrightarrow[-2Et_3\overset{+}{N}H\bar{B}F_4]{2Et_3N\cdot BF_3} (CF_3)_2C{=}C{=}C(COOR)_2$$

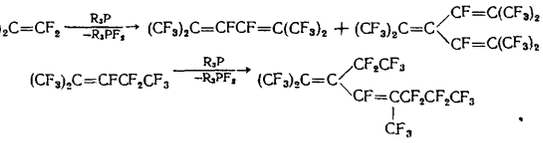
It is of interest that perfluoroisobutene itself plays the role of the dehydrofluorinating agent in the first of the above reactions; as in many other instances,[11,22,91–96] in the second reaction an unusual reagent, namely the triethylamine–boron trifluoride adduct,¶ has been used successfully for the smooth elimination of HF.

The reaction of the highly electrophilic fluoro-olefins with trialkyl phosphites yielded stable adducts—phosphoranes with a P–F bond, which are cleaved only on heating. Depending on the structure of the "fluoro-olefin" component of the phosphorane, its cleavage proceeds either in the direction of the Arbuzov reaction or follows an unusual pathway with formation of a compound of tervalent phosphorus and a fluorine-containing keten acetal:[11]




In the latter case the nucleophile ($RO^-$) attacks the highly electrophilic β-carbon atom of the "acrylic" system, which ultimately leads to the cleavage of the C–P bond.

When perfluoro-olefins were acted upon by tertiary phosphines, interesting reactions were observed, including the defluorodimerisation and defluorotrimerisation reactions,[15,22,98] for example:

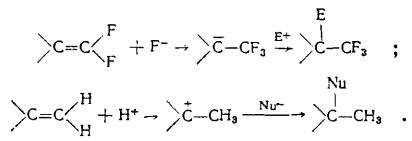


These reactions probably involve the intermediate formation of phosphorus ylides of the type $(CF_3)_2C=C=PR_3$ and $(CF_3)_2CFC(C_2F_5)=PR_3$ (cf. Stepanov and co-workers[65,67]).

¶ The dehydrofluorinating effect of the $Et_3N.BF_3$ adduct has been used to develop a new and apparently most convenient method of synthesis of derivatives of perfluoromethacrylic acid (potential monomers).[11] Other dehydrofluorinating agents are as a rule unsuitable in this case. The same adduct can sometimes be employed also to eliminate an alkyl fluoride, for example, in the conversion of trialkoxyhexafluoroisopropylidenephosphoranes $(CF_3)_2C=P(OR)_3$ into the "phosphorus analogues" of perfluoromethacrylates—the pentafluoroisopropenylphosphonates $CF_2=C(CF_3)PO(OR)_2$.[97]

Since the electron can play the role of a kind of "nucleophile", electrophilic fluoro-olefins undergo electrochemical reduction comparatively readily.[87,99-101] The study of the polarographic behaviour of fluoro-olefins† [87,100,101] showed that the reduction potential decreases with increase of the number of electron-accepting perfluoroalkyl groups at the C=C bond. A correlation was observed between the reduction potential of the fluoro-olefin and the energy of the lowest unoccupied molecular orbital (calculation by the MNDO method).[100,101]

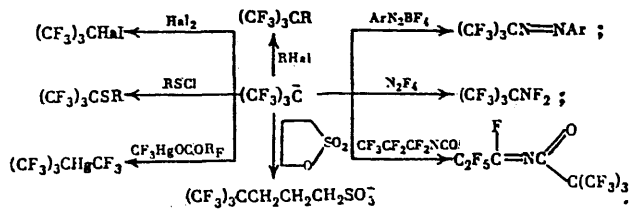
When the $F^-$ anion is used as the nucleophile, the corresponding fluorocarbanions are obtained from perfluoro-olefins. Reactions involving the intermediate formation of fluorocarbanions occupy a notable place in the chemistry of fluoro-olefins.[33,35,102,103] As frequently happens in organofluorine chemistry, a "reverse analogy" obtains here between the reactions of the fluoro-olefins in the presence of the $F^-$ anion and the reactions of non-fluorinated olefins in the presence of the $H^+$ cation (or a Lewis acid):[104]



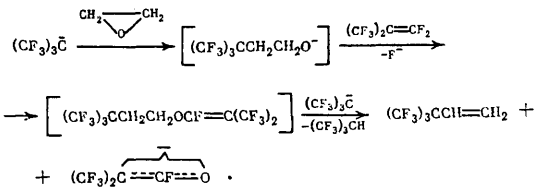
The main contribution made by the Laboratory of Organofluorine Compounds at the Institute of Organoelemental Compounds to this important field involved the study of the reactivity of highly branched fluorocarbanions (in particular the perfluoro-t-butyl anion[12,22] and the perfluoro-t-hexyl anion[57,105-107]), the development of the "nucleophilic mercuration" of fluoro-olefins,[12,22] the development of the chemistry of mesomeric fluorocarbanions,[7,24] the discovery of new sources of the weakly solvated $F^-$ anion containing carbonium counterions,[108] the detection of fluorocarbanions by NMR,[12,109] and the involvement of fluorocarbanions in new types of reactions—azocoupling,[12,107] difluoroamination,[12] sulphenylation,[22] coupled addition to fluoro-olefins,[22,110] reactions with geminal and vicinal dihalogenopolyfluoroalkanes,[22,106,111] etc.

The reactions of branched fluorocarbanions are extremely varied—see, for example, Scheme 1.[12,112,113] Together with subsequent reactions of the products, these reactions lead to extensive possibilities for the synthesis of organofluorine compounds, including potential monomers and surfactants.

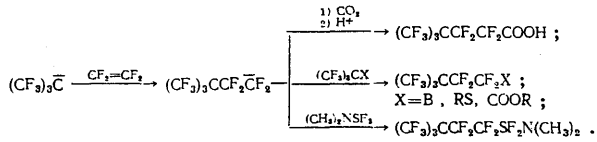
Scheme 1



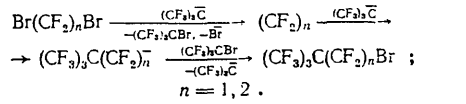
Interesting reactions take place between the carbanions $(CF_3)_2\bar{C}CF_2R_F$ ($R_F$ = F or $CF_3$) and epoxides.[12,24,105] Under certain conditions, the fluoro-olefin can play in this case the role of not only the dehydrofluorinating agent but also of a kind of dehydrating agent, for example:



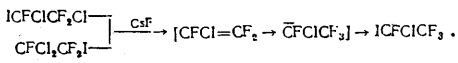
The reaction involving the coupled addition of the perfluoro-t-butyl anion and electrophiles to fluoro-olefins has been discovered recently.[22,110] It leads to ways of synthesising various functional-group substituted organofluorine compounds, for example:



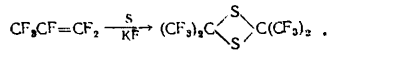
The coupled addition of the anion $(CF_3)_3C^-$ and bromine to tetrafluoroethylene also takes place in the intermediate stages of the reaction of the perfluoro-t-butyl anion with 1,2-dibromotetrafluoroethane, which leads to the substitution of one of the bromine atoms by the $(CF_3)_3C$ residue.[22] The reaction begins with the halogenophilic attack by the tertiary carbanion on the bromine atom of the vicinal dibromo-compound and is completed by a similar attack by the primary carbanion on the bromine atom in perfluoro-t-butyl bromide (or the initial vicinal dibromo-compound). Analogous reactions have been observed also in the reaction with a geminal dibromo-compound—dibromodifluoromethane.[22,106] Tetrafluoroethylene and difluorocarbene are formed respectively as intermediates in the reactions involving the vicinal and geminal dibromo-compounds:



Similar elimination–addition reactions have been observed also on treatment with other nucleophiles of organofluorine compounds containing halogen atoms other than fluorine in the vicinal positions. When the $F^-$ anion is used, the formal result of such a reaction is the substitution of one of the halogen atoms by fluorine, which is accompanied in certain cases by a rearrangement,[111] for example



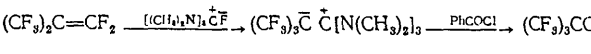
The reactions of fluorocarbanions with sulphur lead to fluorine-containing sulphides, disulphides, trisulphides, dithiacyclobutanes and trithiacyclopentanes.[12] In particular, a convenient method of synthesising the hexafluorothioacetone dimer has been discovered:#



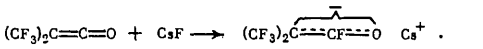
New effective sources of the fluoride anion, namely α-fluoroalkylamines, in which this anion is stabilised by organic cations, were found in subsequent years.[22,108,115] This extends the synthetic possibilities in the chemistry of fluorine-containing anions. Thus the benzoylation of the perfluoro-t-butyl anion has been achieved only when hexamethylguanidinium was used as the counterion:[22]

†The preparative reduction at the cathode via the intermediate formation of mesomeric fluorocarbanions is described below.

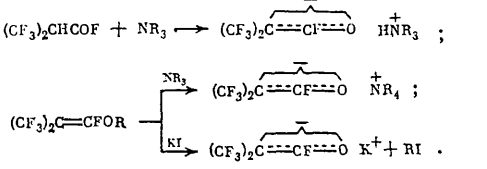
#Subsequently this method was improved.[114]



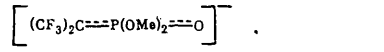
Other fluorine-containing unsaturated compounds react with the fluoride anion like fluoro-olefins (frequently even more readily). Perfluoromethylacryloyl fluoride,[11,24] bis-(trifluoromethyl)keten,[24,76,116] its *N*-benzenesulphonylimine,[91] fluorine-containing allenes,[72,74] and pentafluoroisopropenylphosphonate esters[80] give rise under these conditions to the corresponding stable mesomeric carbanions, for example:



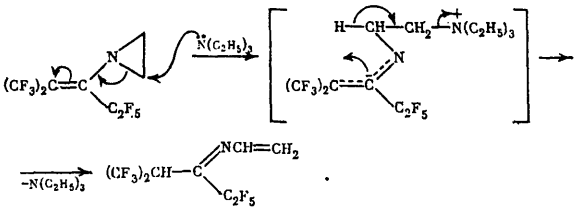
The chemistry of mesomeric fluorocarbanions of this type has been investigated on a fairly wide scale.[2,3,7,24,64] They can be generated not only by the method described above but also from the corresponding CH acids§ and sometimes by the dealkylation of alkyl polyfluoroalkenyl ethers,[2,3,7,24,64,118] for example:



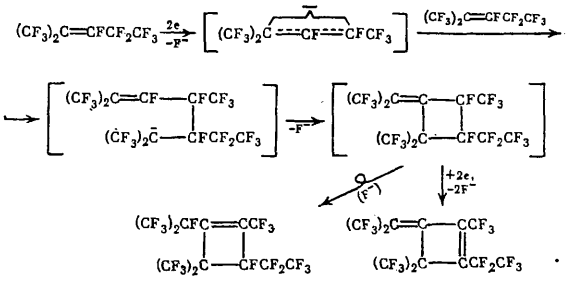
Hexafluoroisopropylidenetrimethoxyphosphorane is dealkylated similarly, forming the anion



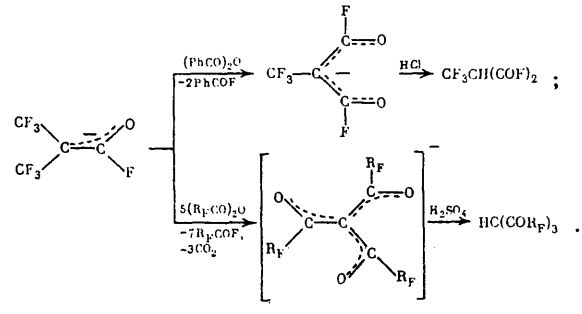
1-Perfluoroalkenylaziridines sometimes behave similarly to alkyl perfluoroalkenyl ethers, manifesting "alkylating" properties in relation to tertiary amines. This is in fact the explanation of the rearrangement of 3-(1-aziridinyl)-perfluoro-2-methylpent-2-ene to 2-hydroperfluoro-2-methyl-3-pentanone *N*-vinylimine:[62]



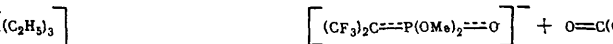
An unusual method of generating mesomeric fluorocarbanions involves the cathodic reduction of fluoro-olefins.[66,87,99] For example, in contrast to the effect of a tertiary phosphine (see above), the preparative electrochemical reduction of the perfluoropropene dimer leads to perfluorinated substituted cyclobutenes as a result of "cathodic dimerisation" involving defluorination and cyclisation. It has been suggested that a mesomeric fluorocarbanion is then formed as an intermediate as a result of the transfer of two electrons to the initial fluoro-olefin and the elimination of the $F^-$ anion:



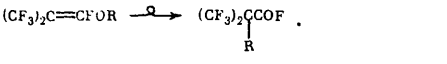
The stable salts formed by the mesomeric fluorocarbanions into a wide variety of reactions—halogenation, alkylation, and partial hydrolysis of the $CF_3$ groups.[2,7,24] On treatment with carboxylic acid anhydrides, the trifluoromethyl groups are converted into fluorocarbonyl or perfluoroacyl groups, which makes it possible to synthesise various di- and tricarbonyl compounds,[24,119] for example:



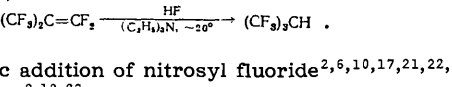
Fluorine-containing α-phosphonate anions enter into the Wittig–Horner reaction with carbonyl compounds:[80]



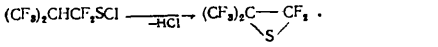
Mesomeric fluorocarbanions are formed as intermediates in the rearrangement of alkyl polyfluoroalkenyl ethers to the fluoride of α-alkyl-substituted carboxylic fluoroacids in the presence of catalytic amounts of a tertiary amine:[7,24]



Certain reactions of perfluoro-olefins with the intermediate formation of fluorocarbanions constitute characteristic examples of the inversion of the addition mechanism, where reagents usually regard it as electrophiles react via a nucleophilic mechanism. Thus, hydrogen fluoride readily adds to perfluoroisobutene in the presence of bases[6,10,12,22] (cf. Brice et al.[120]):

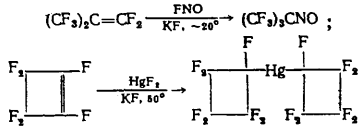


The nucleophilic addition of nitrosyl fluoride[2,6,10,17,21,22,121] or mercury fluoride[2,12,22] to electrophilic fluoro-olefins in the presence of the $F^-$ anion belongs to reactions of the same type,¶ for example:



§Not only mesomeric but also perfluoroalkylcarbanions can be obtained by the heterolysis of the C–H bond. Thus it has been shown for the first time in relation to monohydroperfluoroisobutane $(CF_3)_3CH$ that the proton mobility of the hydrogen atom in monohydroperfluoroalkanes can find a synthetic application.[12,24,117] The intramolecular sulphenylation of β-hydroperfluoroisobutylsulphenyl chloride led to a perfluorinated thiiran:[31]

¶The inversion of the mechanisms takes place also in other cases. Thus, it has been found unexpectedly that highly electrophilic fluorine-containing unsaturated compounds very readily undergo the Prilezhaev epoxidation in ethereal solvents[11,24,122] and are halogenated in acetonitrile.[22,78] Evidently in this case even the use of weakly basic solvents is sufficient to shift the reaction from the usual electrophilic mechanism to a "nucleophilic track".

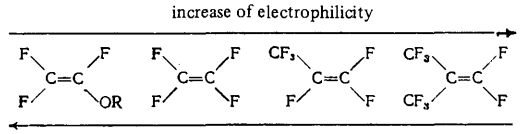


However, the interaction of nitrosyl fluoride with polyfluoroethylenes is catalysed by boron trifluoride in contrast to the analogous reactions of perfluoropropene and perfluoroisobutene:[6]

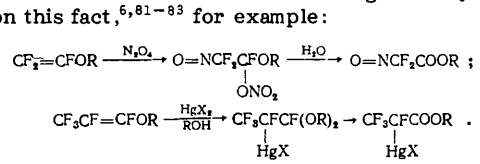


This example shows that reactions via the electrophilic mechanism usual for olefins are possible also in the case of fluoro-olefins.[2,10,21] Such reactions have been little investigated in the first stage of the study of the reactivity of fluoro-olefins, where attention was concentrated on the interaction with nucleophiles. At the same time, despite their low reactivity (or more correctly precisely because of it), fluoro-olefins have advantages in reactions with strong electrophiles over the usual non-fluorinated olefins because the replacement of hydrogen atoms by fluorine atoms as a rule prevents undesirable side processes—oxidation, polymerisation, etc.

The wide-scale study of the reactions of fluoro-olefins with nucleophiles and electrophiles made it possible to generalise the results obtained and to formulate the thesis of the electronically amphoteric character of the double bond in these compounds.[2,4,6] The order in which the electrophilic properties of fluoro-olefins are enhanced and the nucleophilic properties are correspondingly diminished can be accounted for by the electron-accepting effect of the fluorine atoms and the trifluoromethyl groups and also by the electron-donating mesomeric effect of fluorine atoms (and, in the case of alkyl polyfluoroalkenyl ethers, also the oxygen atoms) in the vinyl position acting in the opposite direction:

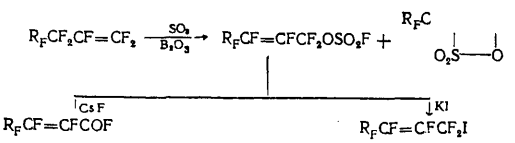



The reactions with electrophiles are more characteristic of the first members of this series than the last. Such reactions are achieved particularly readily for fluoro-olefins containing electron-donating substituents. The use of alkyl polyfluoroalkenyl ethers for the synthesis of a wide variety of derivatives of fluorine-containing carboxylic acids is based on this fact,[6,81-83] for example:



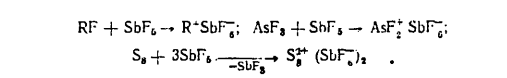
Under fairly severe conditions, strong electrophiles also react with very weak nucleophilic perfluoro-olefins. A typical example is provided by the interaction with sulphur dioxide, which leads to the corresponding cyclic adducts—β-sultones and pyrosultones; these compounds exhibit a varied reactivity and their reactions lead to a wide variety of sulphur-containing organofluorine compounds.[2,123]

It has been shown recently[124-126] that another reaction, substitutional sulphotrioxidation, takes place together with cycloaddition in the presence of Lewis acids. The perfluoroallyl fluorosulphates formed have been used successfully in the synthesis of various fluorine-containing unsaturated compounds—iodides, derivatives of carboxylic acids, dienes, organomercury compounds, etc.[79,127-129], for example:

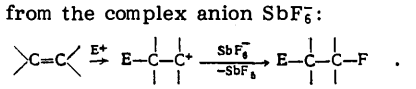


The use of antimony pentafluoride as the Lewis acid makes it possible to obtain fluorosulphates not only from terminal but also from internal fluoro-olefins.[130]

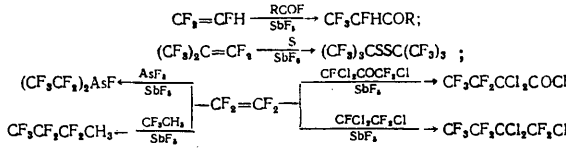
In general the reactions of fluoro-olefins in the presence of antimony pentafluoride are of great interest. Antimony pentafluoride is a very strong Lewis acid, exhibiting in addition oxidative properties, which is capable of generating cationoid species from various reagents,[2,131] for example:



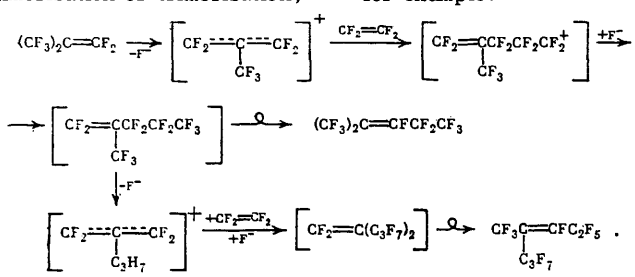
Highly electrophilic cationoid species attack the molecule of a fluoro-olefin and the resulting carbonium ions abstract a fluoride anion from the complex anion $SbF_6^-$:



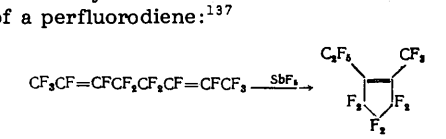
Such reactions have led to extensive synthetic possibilities,[2,68,132-136] for example:



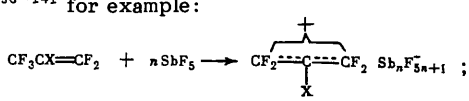
Reactive cationoid species (carbonium ions) can be formed not only from an acyl halide, a halogenoalkane, or a halogenoketone but also from a fluoro-olefin on treatment with $SbF_5$ as a result of the elimination of the fluoride anion from the allyl position. The resulting fluorine-substituted allyl cations can react with another molecule of the fluoro-olefin, which entails dimerisation and, in the case of different olefins, mixed dimerisation or trimerisation,[68,136] for example:



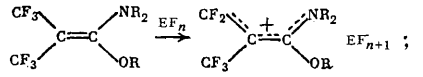
Intramolecular cyclisation has been observed similarly in the case of a perfluorodiene:[137]



Fluorine-containing polyhalogenoallyl cations proved to be so stable in a number of instances that they could be detected by NMR,[138-141] for example:

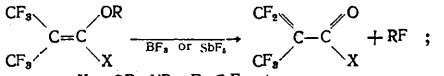


The mesomeric carbonium ion intermediate can be isolated in the form of a salt in the reaction of a Lewis acid with a fluoro-olefin having electron-donating substituents:[11]



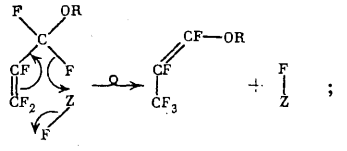
$EF_n = BF_3, SbF_5$ .

Such cations are evidently formed as intermediates in the electrophilic elimination of alkyl fluorides from alkyl polyfluoroalkenyl ethers on treatment with Lewis acids. This reaction is used to synthesise αβ-unsaturated fluorocarbonyl compounds,[2,11,142] for example:



X = OR, $NR_2$, F, $C_2F_5$, etc.

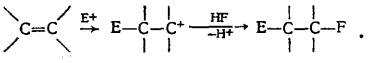
The rearrangement of perfluoroallyl ethers to perfluoropropenyl ethers is also catalysed by fluorine-containing Lewis acids.[143] A synchronous cyclic mechanism has been proposed for this reaction:



R = Alk, Ph; ZF = $BF_3$, RCOF .

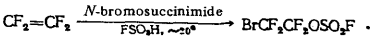
The driving force in this and similar rearrangements is the energy gain resulting from the formation of compounds with a more conjugated bond system.

Apart from Lewis acids, hydrogen fluoride can also be used as the catalyst for the generation of the cationoid species and as a source of $F^-$ anions. The coupled addition of various reagents in HF to olefins, including fluoro-olefins, is of considerable synthetic value:[19]



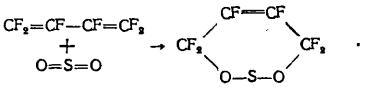
Fluoronitration, fluorohydroxymethylation, fluoroaminomethylation, fluorohydroxylation, etc. products have been obtained in this way.

The coupled electrophilic addition of a halogen and the fluorosulphonic acid residue to fluoro-olefins proved to be a convenient method of synthesis of halogenopolyfluoroalkyl fluorosulphates,[144] for example:

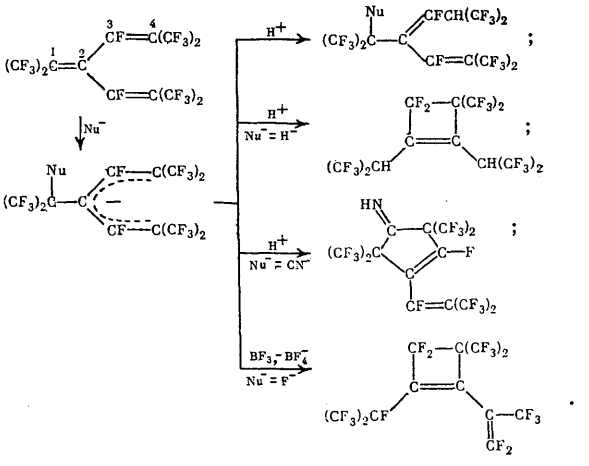


The compounds obtained are of interest as intermediates in the synthesis of derivatives of carboxylic chloro- and bromoperfluoroacids.

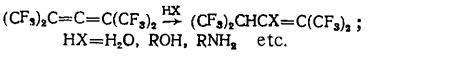
Interesting data have been obtained in the study of the reactivity of fluorine-containing dienes. In the reactions of perfluorobuta-1,3-diene with nucleophiles, π,π-conjugation is usually not observed in the diene molecule.[6]† However, the photochemical or thermal reactions of perfluorobuta-1,3-diene with substituted styrenes or phenylacetylene afford mixtures of cyclic [2 + 2]- and [4 + 2]-adducts apparently as a result of a stepwise biradical reaction.[69,70] The 1,2- and 1,4-cycloaddition products are also formed as a result of the photochemical reaction with sulphur dioxide;[71] however, in the latter case sulphur dioxide reacts in a completely unusual manner, serving as the source of the –O–S–O fragment and not –O–S(=O)–; a new type of heterocyclic compound was thereby obtained—a seven-membered cyclic ester of sulphoxylic acid:



The interaction of the cross-conjugated perfluorotriene with nucleophiles involves 1,4-addition, the attack by the nucleophilic species being directed to the C(1) atom.[146] In certain cases the carbanionic intermediate is stabilised by cyclisation:[147,148]

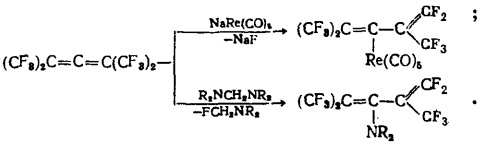


The cumulated perfluorodiene (perfluorotetramethylallene) proved to be extremely reactive. It readily combines with nucleophiles:[2]



HX=$H_2O$, ROH, $RNH_2$ etc.

It is of interest that the 1,2-diene system of this compound cannot as a rule be converted into the conjugated 1,3-diene system.[2] The reactions with trialkyl phosphites, the anions of metal carbonyls, and tetraalkylmethylenediamines are exceptions,[149,150] for example:



## III. POLYFLUOROCARBONYL COMPOUNDS AND THEIR ANALOGUES

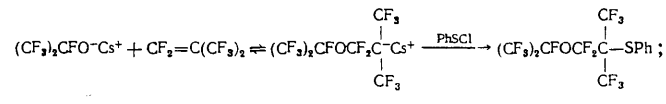
An extensive cycle of studies carried out at the Laboratory of Organofluorine Compounds of the Institute of Organoelemental Compounds has been devoted to the investigation of the influence of fluorine-containing groups on the reactivity of heteroatomic multiple bonds. These studies have made a decisive contribution to the investigation of the chemical properties of fluorine-containing ketones, ketens, and their derivatives, as well as analogues of carbonyl compounds such as aliphatic fluoronitroso- and fluoronitro-compounds.

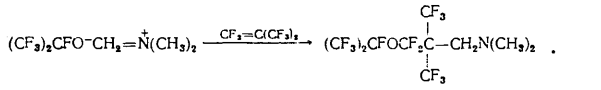
† Perfluorodimethylbuta-2,3-diene behaves analogously.[145]

The introduction of perfluoroalkyl groups enhances the electrophilic properties and diminishes the nucleophilic properties of the multiple bonds. Furthermore, perfluoroalkyl groups increase the stability of the corresponding compounds and a wide variety of derivatives obtained on their basis, so that structures which are unstable or do not exist at all in the "usual" organic chemistry become entirely stable. The most striking example is provided by the stable enol of pentafluoroacetone[25,151] (see below). Geminal diols, hydroxyamines, and diamines are all compounds whose existence conflicts with the El'tekov–Erlenmeyer rule, being stable in the series of organofluorine compounds.[18] Furthermore, unusual structures such as those of the "enols" of *N*-fluoroamides,[152] *N*-fluoroazoxy-compounds,[17] and many others are entirely stable.

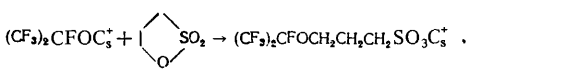
All these findings impart a considerable variety of fluorocarbonyl compounds and their analogues, which entails not only a radical change in their reactivity in the usual reactions but also the appearance of the possibility of reactions which are completely atypical of non-fluorinated compounds. In this Section we shall consider mainly reactions of the latter type.

In contrast to the non-fluorinated ketones, perfluoroketones and their derivatives yield relatively stable adducts with alkali metal fluorides[16,33,35,153] or with α-fluoroalkylamines.[108] The α-fluoroalkoxides formed can in principle add to fluoro-olefins, but this reaction is reversible and the equilibrium is displaced towards the initial reactants. Nevertheless, the formation of the adduct, a perfluoroalkoxycarbanion, has been detected by reactions with electrophiles such as halogens, sulphenyl halides, or the methyleneimmonium cation:[22,108]

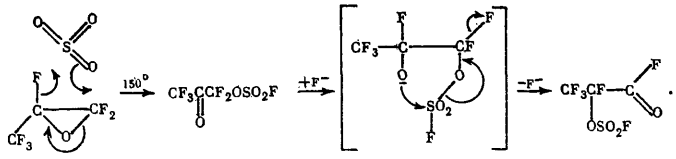




On reaction with propane sultone (1,2-oxathiolan 2,2-dioxide), α-fluoroalkoxides give rise to perfluoroalkoxy-substituted sulphonates, which are of interest for the synthesis of surfactants:[113]

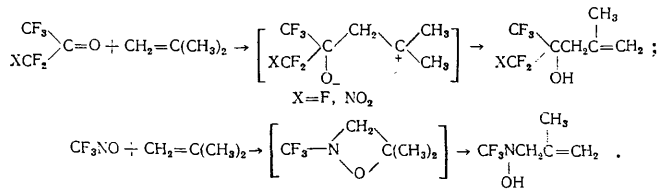


The rearrangement of the fluorosulphate derived from hydroxypentafluoroacetone into α-formylperfluoroethyl fluorosulphate under the influence of the $F^-$ anion has been accounted for by the intermediate formation of a α-fluoroalkoxide and its intramolecular acylation:[2,154]

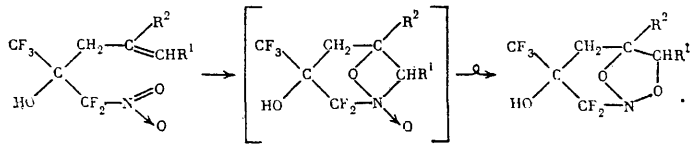


A certain analogy in the reactivities of ketones, ketens, and nitroso- and nitro-compounds is most conveniently traced in relation to stable polyfluoro-compounds, because aliphatic ketens and nitroso-compounds without fluorine are unstable.

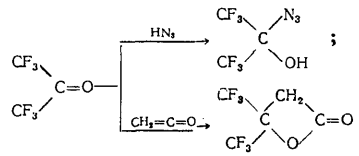
Perfluoroketones,[18,155] bis(trifluoromethyl)keten,[20] and perfluoronitrosoalkanes[17] react with a weak nucleophile such as isobutene in the cold and, in contrast to the non-fluorinated analogues, without catalysts:



The nitro-group reacts similarly with an olefinic double bond but the cyclic adduct formed initially isomerises in this case to a derivative of 1,3,2-dioxazolidine:[156]

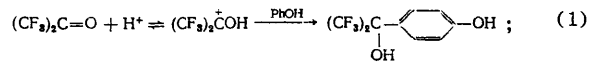


Hydrazoic acid and a keten readily interact with perfluoroketones in the absence of a catalyst[18] whereas their reactions with non-fluorinated ketones take place only in the presence of acids (protic or aprotic):[18]

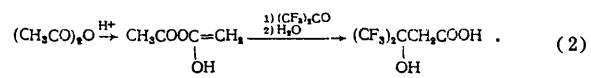


Thus it has been found that increase of electrophilic reactivity and a decrease of nucleophilic reactivity entail the "inversion" of the reaction mechanism: electrophilic addition (for non-fluorinated ketones) is transformed into nucleophilic addition (for perfluoroketones). It is of interest to note that trifluoroacetone reacts with keten only in the presence of $BF_3$ and the reaction proceeds with difficulty compared with the reaction involving acetone. Evidently the presence of one trifluoromethyl group is insufficient to convert the ketone from a nucleophile into an electrophile.[18]

Despite the highly electrophilic properties of perfluorocarbonyl compounds, they are frequently incapable of reacting with very weak nucleophiles. In such cases success has been achieved with the aid of acid catalysis; the catalyst then activates either the fluoroketone [Eqn.(1)] or the attacking agent [Eqn.(2)], for example:[18]



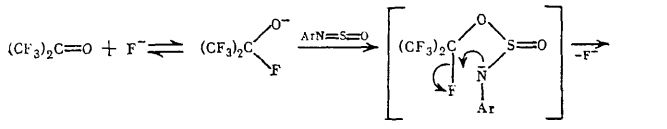
(1)



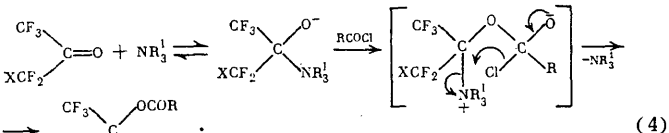
(2)

In view of the reduced basicity of fluoroketones and their derivatives, electrophilic addition of type (1) is difficult.[18]

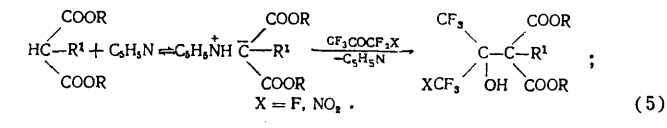
The use of basic catalysts in reactions with electrophiles proved to be no less successful. As in acid catalysis, the basic catalyst can activate either the fluorocarbonyl compound, by converting it into a nucleophilic α-substituted alkoxide [Eqns.(3) and (4)] [157–159] (cf. Zeifman et al.[160]), or the attacking agent, by converting it into a nucleophilic conjugate base [Eqn.(5)]:[18]



(3)

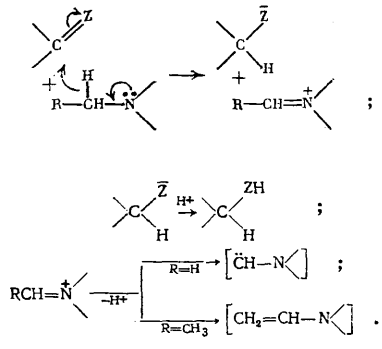


(4)



(5)

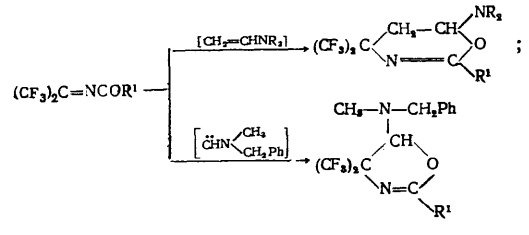
The very high electrophilicity of the C=O groups in fluoroketones[18] and in derivatives of carboxylic fluoroacids,[2,161] of C=N groups in hexafluoroacetone acylimines,[162,163] and of the C=C bond in perfluorotetramethylallene[2] is manifested in oxidation-reduction reactions with tertiary amines. The first stage of these reactions yields an immonium cation, which can be subsequently transformed into an aminocarbene or a vinylamine:



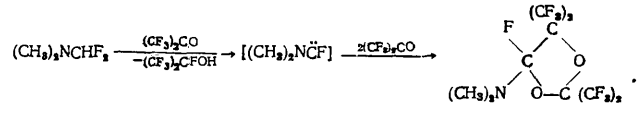
The intermediate formed reacts subsequently with the initial electrophilic fluorine-containing unsaturated compound, for example:

$$[CH_2{=}CHNR_2] + R_FCOX \rightarrow R_FCOCH{=}CHNR_2 .$$

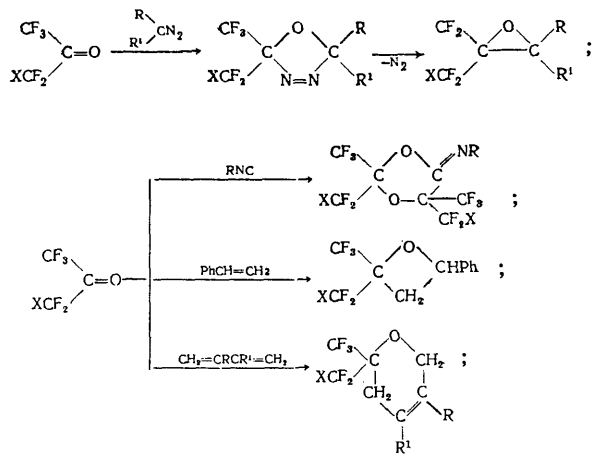
Hexafluoroacetone acylimines give rise to cyclic adducts under these conditions:

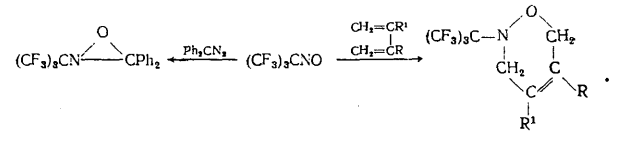


The aminocarbene obtained as a result of the dehydrofluorination of the αα-difluoroalkylamine by the perfluoroketone also undergoes cycloaddition to the initial ketone to form a 1:2 adduct:[115]

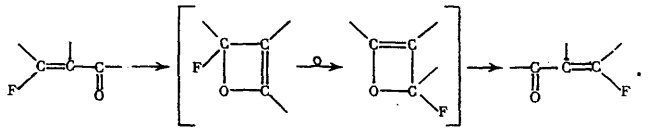


Cycloaddition reactions are in general very characteristic of fluorine-containing ketones[18,164] and ketens,[20] trifluoropyruvate esters,[165] and fluoronitrosoalkanes,[17] for example:

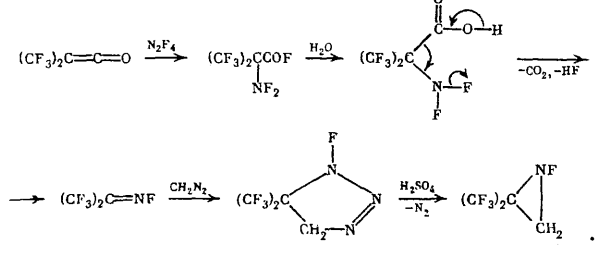




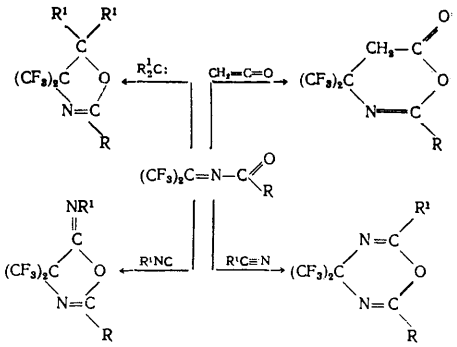
The carbonyl group can also add intramolecularly to the C=C double bond in certain fluorine-containing αβ-unsaturated carbonyl compounds. This entails a kind of rearrangement as a result of which the oxygen and fluorine atoms change places:[11,166]



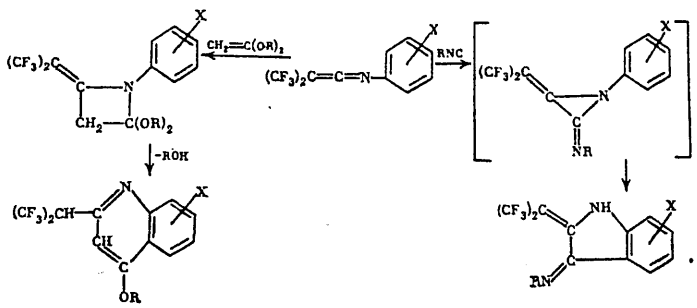
Fluoroketone imines also enter into cycloaddition reactions with dienes and diazo-compounds.[16,167] Imines with electron-accepting substituents both at the carbon atom and at the nitrogen atom are particularly active. For example, hexafluoroacetone *N*-fluoroimine, which is readily obtained from bis(trifluoromethyl)keten, reacts with diazomethane at −50 °C:[152]



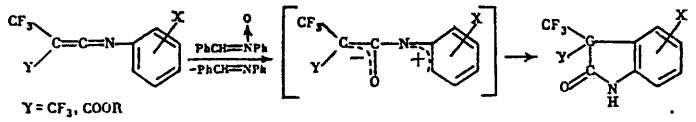
Fluoroketone *N*-acylimines are very reactive, typically undergoing 1,4-dipolar cycloaddition reactions with diazomethane, carbenes, isonitriles, and compounds containing the C=C, C≡C, C=O, and C≡N multiple bonds:[16,168]



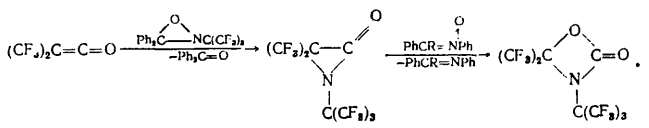
Cycloaddition reactions involving the aromatic ring have been discovered for bis(trifluoromethyl)keten *N*-arylimines. These reactions resemble structurally the Diels–Alder reactions, i.e. keten *N*-arylimines formally behave in this instance like 1,4-dipolar compounds. However, a two-stage mechanism rather than a synchronous mechanism is more likely for reactions of this type, where one of the double bonds of the 1,3-diene forms part of an aromatic ring: betaines or small rings are formed initially, being subsequently stabilised as a result of the reaction with the aromatic ring,[13,169] for example:



The unusual reaction of keten *N*-arylimines with nitrones, which in this instance play the role of oxygen sources, belongs to the class of reactions of this type:[13,169,170]

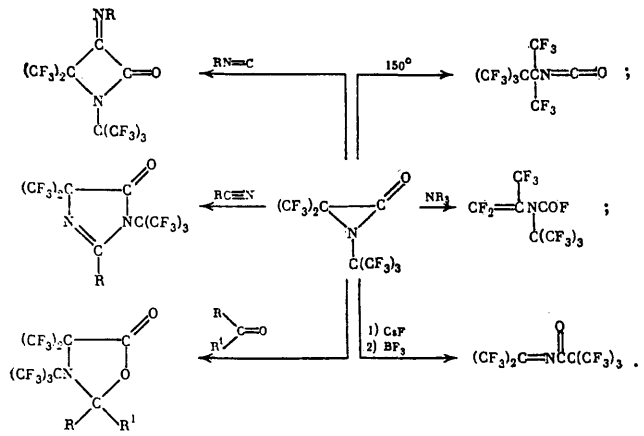


Nitrones react as oxidants also with the uniquely stable perfluoro-α-lactam, which is obtained by the epimination of bis(trifluoromethyl)keten:[27]



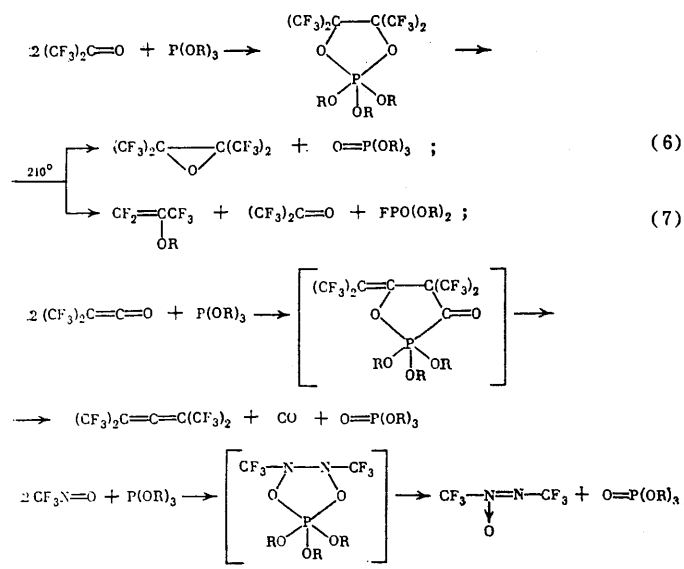
Any of the bonds of the three-membered ring can be ruptured in the cycloaddition reactions with perfluoro-α-lactam, four- or five-membered heterocycles with two heteroatoms being formed. On treatment with nucleophiles ($NR_3$, CsF) or after prolonged heating, perfluoro-α-lactam rearranges to linear isomers: a perfluoroalkyl isocyanate, an unsaturated carbamoyl fluoride, and a ketone acylimine; similar rearrangements of non-fluorinated α-lactams are unknown[28,29] (Scheme 2).

Scheme 2



The analogy between the properties of fluorine-containing ketones, ketens, and nitroso-compounds is manifested particularly strikingly in the isotypical nature of the reactions with phosphite esters. Thus it has been shown that triethyl phosphite reacts in the cold with perfluoroketones,[18] bis(trifluoromethyl)keten,[20] and trifluoronitrosomethane,[17] forming "pinacolisation" products, which decompose in the last two cases already under the conditions of the synthesis (Scheme 3).

Scheme 3



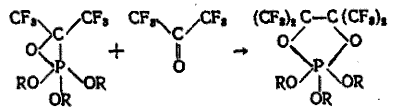
The cyclic phosphorane formed from hexafluoroacetone decomposes only on heating and the reaction proceeds via two pathways [Eqns.(6) and (7)]; the second decomposition pathway [Eqn.(7)] is analogous to the formation of oxime ethers from secondary perfluoronitrosoalkanes:[17]

$$(CF_3)_2CFNO + P(OR)_3 \rightarrow (CF_3)_2C{=}NOR + FPO(OR)_2 .$$

A complete analogy has been observed between the Allen reactions of α-chloroperfluoronitrosoalkanes and the Perkow reactions of α-chlorofluoroketones.[17]

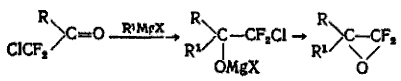
The first step in all these reactions involves the attack by the phosphite on the electrophilic carbon or nitrogen atom.[17,18] The strained three-membered cyclic phosphorane formed then either isomerises or combines with the next molecule of the unsaturated electrophile with rupture of the

C–P and not the P–O bond[18] (as in the decomposition of the four-membered cyclic intermediates in the Wittig reaction), for example:

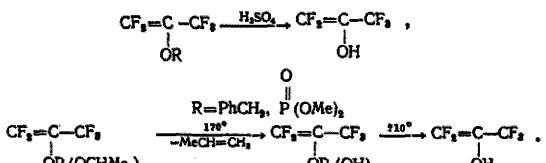


In the reaction with phosphites, two molecules of the fluorine-containing ketone or keten therefore combine with one another via the formation of a C–C bond, in contrast to the reaction with isonitriles, in which a C–O bond is formed.[8,18]

The trifluoromethyl groups in hexafluoroacetone and its derivatives are inert and do not react.# Although this restricts the synthetic possibilities of perfluoroketones, it is nevertheless convenient in the sense that the reactions of carbonyl groups are not complicated by the involvement of the other reaction centres of the molecule.[18] However, the replacement of one or several fluorine atoms by chlorine appreciably "activates" the fluoroalkyl groups, so that chlorofluoroketones are able to enter into the Perkow reaction.[25] It has been found that the chlorine atoms also readily undergo intramolecular nucleophilic substitution in the alkoxides of tertiary polyfluorocarbinols.§ This resulted in the formation of a wide range of polyfluorinated epoxides:[2]

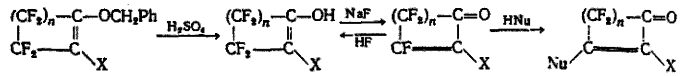


An outstanding investigation by Knunyants, Dyatkin, and Bekker and co-workers was devoted to metastable enols. It is known[25] that pentafluoroacetone $HCF_2COCF_3$ does not enolise because of its low acidity (the greater thermodynamic stability of the keto-form of pentafluoroacetone compared with the enolic form has been confirmed by a non-empirical calculation by the SCF method[172]). However, it has been found that the corresponding enol (pentafluoro-2-propenol) is entirely stable and can be obtained by the acid hydrolysis of benzyl pentafluoroisopropenyl ether or dimethyl pentafluoroisopropenyl phosphate or by the thermolysis of diisopropyl pentafluoroisopropenyl phosphate:[25,151,173]



The first representative of the sterically unhindered metastable enols was synthesised in this way. The exceptionally high kinetic stability of this compound can be accounted for by the optimum combination of its properties. Pentafluoro-2-propenol manifests, on the one hand, a relatively low kinetic acidity as a consequence of the destabilisation of the corresponding anion due to the mesomeric electron-donating effect of the vinyl fluorine atoms and, on the other hand, it exhibits a low proton affinity owing to the electron-accepting effect of the fluorine-containing group.[25,174] Certain other aliphatic polyfluoroenols, for example, 3-chlorotetrafluoro-2-propenol $CF_2 = C(OH)CF_2Cl$ or nonafluoropent-2-en-3-ol $CF_3CF = C(OH)C_2F_5$ also proved to be entirely stable.[25,174]

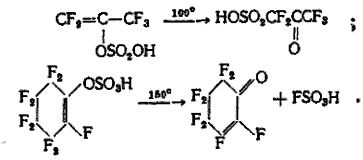
Alicyclic fluorine-containing enols have been likewise synthesised.[25,175] Their most characteristic feature is their ready dehydrofluorination by weak bases and subsequent "vinyl" substitution of the β-fluorine atom:[25,173,175,176]



X = H, F; $n = 1-3$; Nu = RO, $R_2N$.

It is of interest that the dehydrofluorination is reversible, thus confirming experimentally the hypothesis of the 1,4-addition of hydrogen halides to αβ-unsaturated carbonyl compounds.[173,177]

A general property of the aliphatic and alicyclic enols obtained is their ability to give rise to *O*-derivatives as a result of the substitution of the mobile hydrogen atom by an alkyl, acyl, or sulpho-group. Pentafluoropropenyl sulphate isomerises to a sulphoketone on heating, while an alicyclic sulphate eliminates fluorosulphonic acid:[25,176]



Pentafluoro-2-propenol gives rise also to other O-derivatives, namely $CF_2 = C(CF_3)OX$ (X = Li, $R_3Si$, $R_3Ge$, $R_3Sn$, or $R_2P$) or the *C*-derivatives $XCF_2COCF_3$ (X = halogen, NO, ArN = N, or RHg).[25,178] When mercuripentafluoroacetone is treated with acids, the initial enol is regenerated; the transfer of the reaction centre in the protodemercuration of α-mercuricarbonyl compounds, suggested previously, has thus been confirmed.[25,178]

The metastable pentafluoro-2-propenol isomerises wholly to pentafluoroacetone on prolonged heating at 180 °C and also in the presence of weak bases.[25,173]¶ In contrast to this, α-hydrohexafluoroisobutyraldehyde $(CF_3)_2CHCHO$ is involved in a tautomeric equilibrium with the corresponding enol, whose content increases (up to 100%) with increase of the basicity of the solvent.[7] The presence of the electron-accepting trifluoromethyl groups greatly increases, as was to be expected, the tendency towards enolisation in this instance.

However, it has been found that in the case of bis-(perfluoroacyl)methanes, the introduction of perfluoroalkyl or perfluoroacyl groups has the opposite effect, causing a sharp suppression of the enolisation, so that the compounds $(R_FCO)_2CHCF_3$ exists wholly in the diketone form, while the compound $(C_3F_7CO)_3CH$ exists to the extent of 90% in the triketone form.[119] Evidently the bulky groups prevent the formation of the planar chelate ring of the cis-enol.

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#On the other hand, the mobility of the allyl fluorine atoms in bis(trifluoromethyl)keten and in *N*-perfluoropropyldiphenylketen imine are responsible for the ready isomerisation of these heterocumulenes to 1,3-heterodienes.[13]

§Analogous intermolecular reactions are also known.[171]

¶The metastable enethiol $(CF_3)_2C = C(SH)C_2F_5$ isomerises analogously to the thioketone $(CF_3)_2CHC(=S)C_2F_5$.[179] However, the isomerisation of the corresponding sulphenyl chloride $(CF_3)_2C = C(SCl)C_2F_5$ to the α-chlorothioketone $(CF_3)_2CClC(=S)C_2F_5$ is reversible;[180] a new type of cationotropic tautomerism (chlorotropism) was observed in this instance.

It is of interest that a fairly considerable energy barrier to the enolisation of the metastable diketone form has been observed for heptafluoroacetylacetone $(CF_3CO)_2CHF$. At equilibrium, this β-diketone is 90% enolised[42] in contrast to the wholly enolised hexafluoroacetylacetone $(CF_3CO)_2CH_2$.

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We believe that the foregoing data provide an idea about the extent to which the presence of perfluoroalkyl groups alters the chemical properties of organic compounds. "When one views the path traversed by fluorine chemistry, one sees that many features which previously outraged the chemist's imagination have become commonplace; however, the unusual characteristics of this field of chemistry are so pronounced that it still yields new phenomena and facts, which, on the one hand, expand theoretical ideas in chemistry and, on the other, lead to important practical results. Both these aspects are a source of enormous satisfaction to the investigator".[2]

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# Coupled Chemical Diffusion of Ions and Electrons in Non-stoichiometric Crystals

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The theory of the coupled chemical diffusion of ions and electrons in solids under the influence of the gradient of the degree of deviation from the stoichiometric composition is described consistently on the basis of the phenomenological and statistical-thermodynamic approaches. Within the framework of the model of non-interacting defects, the behaviour of crystals with the following types of disorder is examined: Frenkel', structural, Schottky, Wagner, impurity, and electronic disorder. Account has been taken of the influence of the degeneracy of the electrons. The main principles of the experimental methods for the determination of the coupled chemical diffusion coefficient are described and the experimental data are compared with the theory.
The bibliography includes 85 references.

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## I. INTRODUCTION

Studies of diffusion processes in solids have already had a history extending over a century. Nevertheless, the theory of these processes is still far from being perfect. Perhaps the only exception is that of the simplest type of diffusion, namely self-diffusion, characterising the rate of migration of species in chemically homogeneous substances. Considerable advances in this field have been achieved as a result of the employment of radioactive tracers which are chemically indistinguishable from the principal atoms of the material investigated.

However, when a more complex phenomenon is tackled, namely the diffusion of impurity atoms in a chemically homogeneous substance (heterodiffusion), considerable difficulties arise owing to the need to take into account the correlation factors as a consequence of the different mobilities of the main and impurity atoms, the formation of different kinds of associated species, etc. Finally, the picture becomes very greatly complicated when one considers diffusion in variable-composition chemical compounds (chemical diffusion), otherwise referred to as non-stoichiometric compounds. In non-stoichiometric ionic compounds of the type $M_{1+\delta}X_r$, where $r$ is an integer and $\delta$ the degree of deviation from stoichiometry, the excess content of cations and ions leads to the appearance of excess quasi-free electrons in the conductivity band or of electron holes in the valence band. When a gradient of the deviation from stoichiometry exists in a compound of this kind, the chemical potential gradients of both the metallic and non-metallic components, M and X, under the influence of which the cations and anions diffuse towards one another, are also present under these conditions. The local electroneutrality of the specimen is maintained by the equivalent flux of electrons. Such a process is usually referred to as chemical diffusion but this term requires revision. Strictly speaking, the term "chemical" refers to any diffusion in the field of chemical potentials, including the mutual diffusion of the components of non-ideal solutions. In a narrower sense the phenomena considered in this review will therefore be referred to as the coupled chemical diffusion (CCD) of ions and electrons in a chemical field, due to the deviations of the composition from stoichiometry (DCS), and in the electric field arising owing to the difference between the mobilities of species of different kinds.

The most important characteristic of CCD is the coupled chemical diffusion coefficient $D$, which is determined by the combination of the coefficients of the random diffusion of the cations and anions, the mobilities of the electron carriers, and the non-stoichiometry parameters. All these quantities are related to the defect structure of the crystal in different ways. For this reason, comparison of the CCD coefficient in the DCS field with other transport characteristics makes it possible to construct models of the disorder in crystalline bodies at the atomic level, which is one of the most important tasks of the modern solid state chemistry.

Chemical diffusion plays an important and in many cases also a decisive role in real processes accompanied by solid-phase chemical reactions: processes involving the formation of complex compounds from simpler compounds (the oxidation of metals and the solid-phase synthesis of materials) and the decomposition of complex compounds into simpler ones (the isolation of metals from ores, the purification of materials, etc.) and processes in which matter and electricity are transported in the elements of control systems (solid electrolytes and electrodes in microionics and electrochromic materials in optics) and in power plants (electrolysers and galvanic cells, thermoelectric converters, the electrodes of MHD generators, etc.).

A distinctive feature of the CCD in the DCS field relative to, for example, the self-diffusion of labelled atoms is the extremely high effective diffusion coefficients. Thus, whereas at 1000 K the self-diffusion coefficients are in the range $10^{-15}$–$10^{-8}$ $cm^2\ s^{-1}$ for the majority of crystalline bodies, reaching $10^{-5}$ $cm^2\ s^{-1}$ only in structurally disordered crystals (superionic conductors), the coupled chemical diffusion coefficient (CCDC) of ions, for example, in silver chalcogenides, is $10^{-1}$ $cm^2\ s^{-1}$. Such high values of the CCDC ensure an intense transport of matter for an insignificant driving force, i.e. for a small gradient of the degree of DCS.

The present review is devoted mainly to a consistent description of the theory of the CCD in the DCS field on the basis of ideas described in a monograph.[2] The methods for the measurement of the calculated quantities are also examined and the measured transport parameters of a series

of non-stoichiometric compounds are briefly discussed. The author did not attempt to give a detailed survey of the experimental studies and confined himself to the most reliable data. A more complete bibliography can be found, for example, in a number of other reviews.[3-6]

## II. PHENOMENOLOGICAL EQUATIONS

### 1. General Expressions

For the non-correlated diffusion in solids, where the movement of carriers of different kinds is independent, the flux of charged species of type $k$ in the chemical (concentration) and electrical field is defined by the Wagner equation[7]

$$J_k = -\frac{\varkappa_k}{q_k^2}(\nabla\mu_k + q_k\nabla\varphi) \ . \qquad (1)$$

Here the flux is measured as the number of species passing per unit time through a unit surface in a coordinate system rigidly linked to crystal lattice sites. The symbol $\varkappa_k$ denotes the partial specific electrical conductance of such species, $q_k$ is their charge, and $\nabla\mu_k$ and $\nabla\phi$ are respectively the chemical potential and electrostatic potential gradients. The following expression is equivalent to the above equation:

$$J_k = -\frac{N_k D_k}{kT}(\nabla\mu_k + q_k\nabla\varphi) \ , \qquad (2)$$

where $N_k$ is the concentration (number of $k$ species per unit volume) and $D_k$ the "random" diffusion coefficient of the $k$ species linked to their electrical conductivity $\varkappa_k$ by the Nernst–Einstein relation:[2]

$$kT\varkappa_k = q_k^2 N_k D_k \ . \qquad (3)$$

In contrast to Eqn.(1), Eqn.(2) contains no charge in the denominator and is applicable not only to charged but also to neutral species (atoms, molecules, and defects) with $q_k = 0$.

By virtue of their phenomenological character, Eqns.(1) to (3) are equally valid for two different methods of describing the structure of defective crystals and the set of current carriers present in them.[2,13] In the first case the systems of structural elements, where the mobile carriers are assumed to be atoms or ions, may be adopted as a basis. The corresponding random diffusion coefficients of ions and electrons are referred to as macroscopic.[13] Eqn.(2) is applicable both in the absence of correlation (for example, for the direct intersite transport mechanism and probably in structurally disordered phases), where the values of $D_k$ for atoms and ions are identical with their self-diffusion coefficients $D^*$ measured with the aid of radioactive isotopes, and in the presence of a correlation effect. In the latter case, the quantity $D_k$ in Eqn.(2) is linked to the self-diffusion coefficient by the Heyven relation[8] $D_k = f_k D_k$, where $f_k$ is the correlation factor. In the second case, which is preferable in the statistical description of transport, the mobile carriers are assumed to be the atomic and ionic or electronic defects in the crystal lattice differing in their nature and also in their charge and energy state. The corresponding diffusion coefficients are referred to as microscopic.[2,13]

### 2. Neutral Species

Neutral species diffuse only under the influence of their chemical potential gradient $\nabla\mu_k$ and their diffusion is independent of the electric field. Assuming that, for the known composition of the specimen, the chemical potential of the species $\mu_k$ is a single-valued function of the concentration $N_k$, we can express $\nabla\mu_k$ in the form

$$\nabla\mu_k = \frac{d\mu_k}{dN_k}\nabla N_k = kT\frac{d\ln a_k}{dN_k}\nabla N_k \ ,$$

where $a_k$ is the thermodynamic activity of the $k$ component. Then Eqn.(2) assumes the form of Fick's first equation $J_k = -D_k\nabla N_k$ with an individual chemical diffusion coefficient (ICDC) of species of type $k$:[2]

$$\tilde{D}_k = F_k D_k \ , \qquad (4)$$

where the multiplier

$$F_k = \frac{N_k}{kT}\frac{d\mu_k}{dN_k} = \frac{d\ln a_k}{d\ln N_k} \qquad (5)$$

represents the so-called thermodynamic chemical diffusion factor. In the case of substitutional solid solutions, where $\Sigma N_k = \text{const}$. and $d\ln N_k$ can be replaced by $d\ln c_k$, where

$$c_k = N_k / \sum_k N_k$$

is the atomic fraction of atoms of type $k$ in the corresponding sublattice, Eqn.(5) becomes identical with Darken's equation.[9]

Eqns.(4) and (5) belong to the set of principal equations of the modern theory of chemical diffusion and the calculation of thermodynamic factors is the central task in the latter.

### 3. Ions and Electrons. The General Case

The coupled diffusion of ions and electrons takes place as a rule in an electric field, which is determined both by an external source and by the charge of the moving species. The field accelerates the movement of the less mobile charge carriers and retards that of the more mobile ones. Accordingly, in the general case the role of the electric field in transport processes is just as important as the role of chemical fields. Nevertheless, for further consideration, it is convenient to introduce the concept of the individual chemical diffusion coefficient of charged species of type $k$, defined by the same equations (4) and (5) as for neutral species. The definition of the diffusion coefficient $\tilde{D}_k$, as the ratio of the flux of species of type $k$ to the chemical potential gradient multiplied by $N_k/kT$ subject to the condition that the electric field gradient is zero, follows from Eqn.(2).

In the general case of the coupled diffusion of electrons and several ions of the $k$ type, their fluxes are linked by the condition

$$-eJ_e + \sum_k q_k J_k = I,$$

where $I$ is the electric current density in the specimen. This makes it possible to eliminate the electric field strength from Eqn.(1) for the electron flux:

$$J_e = \frac{-\sigma}{e(\varkappa+\sigma)}\left[I + \sum_k \varkappa_k\left(\frac{\nabla\mu_k}{q_k} + \frac{\nabla\mu_e}{e}\right)\right] \ , \qquad (6)$$

where $\sigma = \varkappa_e$ is the electronic conductivity and $\varkappa = \sum_k \varkappa_k$ the overall ionic conductivity.

Eqn.(6) is phenomenological in character and is therefore applicable to systems containing mobile ions with any effective charges $q_k$, including arbitrarily selected charges. This factor is extremely important because the true ionic charges in solids are frequently unknown. In the calculation of the transport characteristics of the system within the framework of the phenomenological approach, it is more

convenient to choose classical ions as the moving species with the nominal charges $q_k = \pm z_k e$ determined by the valences of the corresponding elements $z_k$. In this case, it follows from the electro-neutrality condition for the crystals $eN_e = \sum_k q_k N_k$ that the valence electrons at a concentration $N_e$, in excess relative to the stoichiometric composition $\left(\sum_k q_k N_k = 0\right)$, participate in the transport regardless of whether these electrons exist in a quasi-free state or are localised at some donor or acceptor centres.

It is convenient to select the concentration of the excess (of deficient) electrons as a measure of the DCS. For example, in the case of a binary crystal $MX_r$ the quantity

$$N_e = z_1 N_1 - z_2 N_2$$

($z_1$ and $z_2$ are the valences of the metal M and the non-metal X) determines the difference between the concentrations of the cations and anions measured in terms of the number of elementary charges per unit volume (equivalent concentration multiplied by the Avogadro number). For the specified overall composition of the specimen, the chemical potential of both its components can be unambiguously related to $N_e$. In the absence of an electric current in the specimen, the expression for the electron flux [Eqn.(6)] can therefore be represented in the form of Fick's first equation $J_e = -\tilde{D}\nabla N_e$ with an effective CCDC:

$$\tilde{D} = t_i \tilde{D}_e + t_e \tilde{D}_i \ , \qquad (7)$$

where

$$t_i = \sum_k t_k = \varkappa/(\varkappa+\sigma)$$

is the overall transport number of the ions, $t_e = \sigma/(\varkappa+\sigma)$ the transport number of the electrons, and $\tilde{D}_e$ and $\tilde{D}_i$ are defined by the expressions

$$\tilde{D}_e = \frac{\sigma}{e^2}\frac{d\mu_e}{dN_e}; \qquad \tilde{D}_i = \sum_k \frac{\varkappa_k}{q_k e}\frac{d\mu_k}{dN_e} \ ,$$

where $\mu_e$ is the chemical potential of the electrons.

The physical significance of these quantities becomes apparent on further transformation. We shall represent the electronic conductivity by the sum of the conductivity due to the movement of $n$- and $p$-type carriers (conductivity electrons and holes): $\sigma = \sigma_n + \sigma_p$. With the aid of the Nernst–Einstein equation, we express the partial conductivities $\sigma_n$ and $\sigma_p$ in terms of the diffusion coefficients of the conductivity electrons and holes:

$$kT\sigma = e^2(nD_n + pD_p),$$

where $n$ and $p$ are their volume concentrations. The partial conductivities $\varkappa_k$ of ions of the $k$th type can also be expressed in terms of their diffusion coefficients:

$$kT\varkappa_k = q_k^2 N_k D_k.$$

Taking into account the evident relation $\mu_e = \mu_n = -\mu_p$, where $\mu_n$ and $\mu_p$ are the chemical potentials of the conductivity electrons and holes, and also the definitions specified by Eqns.(4) and (5), we obtain the equations

$$\tilde{D}_e = \frac{dn}{dN_e}\tilde{D}_n - \frac{dp}{dN_e}\tilde{D}_p; \quad \tilde{D}_i = \sum_k \frac{q_k}{e}\frac{dN_k}{dN_e}\tilde{D}_k \ . \qquad (8)$$

Hence it is seen that $\tilde{D}_e$ is the effective CDC of the electrons averaged with respect to $n$- and $p$-type carriers. The weighting factors $dn/dN_e$ and $-dp/dN_e$ of the ICDC of the electron carriers $\tilde{D}_n$ and $\tilde{D}_p$ in Eqn.(8) determine the contributions of the conductivity electrons and holes to the overall DCS gradient. The coefficients $(q_k/e)dN_k/dN_e$ of the ICDC of the ions $\tilde{D}_k$ have an analogous significance, so that $\tilde{D}_i$ is the effective CDC of the ions averaged with respect to all the ionic species.

An equation similar to Eqn.(7) was first derived[10] for the coupled diffusion of cations and anionic vacancies in a structurally disordered solid electrolyte. Since Grafov and Ukshe[10] used the relations of the thermodynamics of ideal solutions, their equation contained the usual diffusion coefficients of the corresponding species $D_k$ instead of the individual chemical diffusion coefficients $\tilde{D}_k$. A more rigorous derivation of Eqn.(7) taking into account thermodynamic factors was achieved by the author of the present review for the coupled diffusion of two arbitrary kinds of charged species.[1]

A remarkable feature of Eqn.(7) is the close relation between the electrical ($t$) and diffusional ($\tilde{D}$) characteristics of the ions and electrons due to the self-consistent character of the electrochemical fields in the diffusion zone. In the general case, this relation precludes the separation in Eqn.(7) of the individual terms due to the electrical and chemical fields. Such a separation becomes possible only in the limiting cases at $t \to 0$ or $t_e \to 0$, which are considered below.

Eqn.(7) can be conveniently used in the statistical calculation of the CCDC when the thermodynamic factors of the ions and electrons are determined by specific microscopic models of the disorder in the crystal. On the other hand, in the phenomenological approach, these factors remain undefined, because the chemical potentials of the ions and electrons are not susceptible to direct measurement separately. For this reason, within the framework of the phenomenological theory, it is useful to resort to the chemical potentials of the neutral components $A_k$ corresponding to the $k$ ions with the aid of the evident relation

$$\mu_{A_k} = \mu_k + \frac{q_k}{e}\mu_e \ .$$

Under these conditions, a simple and at the same time general formula for the effective CCDC follows from Eqn.(6):

$$\tilde{D} = \sum_k \frac{q_k dN_k}{e\, dN_e}\tilde{D}_{ke} \ . \qquad (9)$$

As in Eqn.(8), the summation for $\tilde{D}_i$ is carried out in this case over all types of ions. The partial quantities $\tilde{D}_{ke}$ have the significance of the CCDC for ions of the $k$ type and electrons and are expressed either in terms of the partial conductivities of the $k$ ions and electrons:

$$\tilde{D}_{ke} = \frac{\varkappa_k \sigma}{q_k^2(\varkappa_k+\sigma)}\frac{d\mu_{A_k}}{dN_k} \ , \qquad (10)$$

or in terms of the transport number of electrons and the macroscopic diffusion coefficients of the $k$ ions:

$$\tilde{D}_{ke} = t_e D_k \frac{d\ln a_{A_k}}{d\ln N_k} \ . \qquad (11)$$

## 4. Ions of One Kind

In the simplest case where mobile ions of only one kind are present and the concentrations of all the remaining ions are constant, the electroneutrality condition is $eN_e = q_k \Delta N_k$, where $\Delta N_k$ is the excess content of the mobile ions relative to the stoichiometric composition. In this case Eqn.(9) assumes the simple form $\tilde{D} = D_{ke}$, which has two important corollaries.

Firstly, for mobile ions of one kind the CCDC is expressed, according to Eqn.(10), in terms of quantities susceptible to direct determination from independent experiments, which leads to the possibility of a rigorous comparison of the phenomenological theory with experiment. The derivation of Eqn.(10) for the case under consideration is due to Yokota,[11] who used it to calculate the transfer of charge in non-stoichiometric compounds of the type of silver sulphide in which the charge carriers are electrons and cations.

Secondly, when mobile ions of only one kind are present, Eqn.(11) for the CCDC of ions and electrons differs from Eqns.(4) and (5) for the ICDC of neutral atoms $A_K$ only by the multiplier $t_e$ and becomes identical with the latter for $t_e \cong 1$, i.e. when the electronic conductivity predominates ($\sigma \gg \varkappa$). In this case the coupled diffusion of ions of the same sign and of electrons is formally equivalent to the diffusion of the corresponding atoms. This conclusion is entirely understandable. Indeed, when $\sigma \gg \varkappa$, electrons exist under virtually equilibrium conditions and can compensate for the charge transfer by ions having low mobilities without much difficulty. The diffusional jumps of ions therefore lead to the same migration of substance as the jumps of neutral atoms and the diffusion in electronic conductors can be described with equal success in terms of the movement of both atoms and ions in the mobile electron medium. This factor is very important for the phenomenological theory of diffusion in solids with an intermediate ionic-covalent character of the bond, for example, in semiconducting compounds of the type $A^{III}B^{V}$, where the exact atomic mechanism of diffusion is usually unknown.

### 5. Ions of Two Kinds in a Binary Compound

We shall now consider a more complex case—the crystal of a binary ionic compound $MX_r$ in which ions of both kinds are mobile. By designating the parameters of the cations and anions by the subscripts 1 and 2 respectively, we obtain $q_1 = z_1 e$ and $q_2 = -z_2 e$. For not unduly large DCS, $r = N_2/N_1 \cong z_1/z_2$ and one can therefore formulate the Gibbs–Duhem relation for the chemical potentials of the components in the form $z_2 d\mu_M + z_1 d\mu_X = 0$. Then, on substituting Eqn.(10) in Eqn.(9), we obtain the following expression:

$$\tilde{D} = \frac{\varkappa\sigma}{z_1 e^2 (\varkappa + \sigma)} \frac{d\mu_M}{dN_e} = -\frac{\varkappa\sigma}{z_2 e^2 (\varkappa + \sigma)} \frac{d\mu_X}{dN_e} \cdot \qquad (12)$$

Substitution of Eqn.(11) in Eqn.(9) leads to equivalent relations:

$$\tilde{D} = t_e N_1 (z_1 D_1 + z_2 D_2) \frac{d\ln a_M}{dN_e} = -t_e N_2 (z_1 D_1 + z_2 D_2) \frac{d\ln a_X}{dN_e} \cdot \qquad (13)$$

Eqns.(12) and (13) are analogous to the familiar Wagner formulae[7] which Wagner derived in connection with the development of the theory of the oxidation of metals.† Like Eqns.(9)–(11), they contain the absolute concentrations of the mobile components, namely the numbers of species per unit volume, as the variables.

Together with the relations quoted, an expression for $\tilde{D}$, incorporating the relative concentrations (atomic fractions) of the components, i.e. $c_1 = N_1/(N_1 + N_2)$ and $c_2 = N_2/(N_1 + N_2)$, is sometimes used in the literature. In terms of these variables, Eqns.(13) assume the simple form

$$\tilde{D} = c_2 \tilde{D}'_{1e} + c_1 \tilde{D}'_{2e} ; \qquad (14)$$

$$\tilde{D}'_{1e} = t_e D_1 \frac{d\ln a_M}{d\ln c_1} ; \quad \tilde{D}'_{2e} = t_e D_2 \frac{d\ln a_X}{d\ln c_2} \cdot \qquad (15)$$

Eqn.(14) is formally identical with Darken's equation[9] for binary metallic alloys (more precisely for atomic substitutional solid solutions—see also Chebotin,[2] p.248). However, the partial coefficients $\tilde{D}'_{1e}$ and $\tilde{D}'_{2e}$, corresponding to the coupled diffusion of cations and electrons or of anions and electrons, differ from the ICDC for neutral atoms [Eqns.(4) and (5)] and from the CCDC [Eqn.(11)] for the diffusion of ions of the same size and electrons even under conditions where $t_e \cong 1$, since in the case considered the cations and anions are distributed in different sublattices and $N_1 + N_2 = \text{const.}$, so that $d\ln c_k \neq d\ln N_k$.

All the equations quoted above were obtained by resorting to some kind of model ideas concerning the microscopic structure and the mechanisms of transport in solids. Their character is therefore phenomenological and they can be applied, in principle, to crystals with any types of disorder and with any types of chemical bonding. The diffusion coefficients of the components $D_k$ and the thermodynamic factors $F_k$ then play the role of phenomenological parameters susceptible either to experimental determination or to calculation on the basis of the microscopic theory. The subsequent exposition will concern the solution of the latter problem within the framework of the statistical-thermodynamic theory of disorder in crystalline bodies.[2]

## III. THE CHEMICAL DIFFUSION COEFFICIENT OF ELECTRONS UNDER CONDITIONS WHERE IONIC DISORDER IS DOMINANT

We shall consider below crystals with dominant ionic disorder—either with structural disorder, where the classical ions are distributed among a large number of sites, or with ionic point defects whose effective charges correspond to the state of total ionisation. In all cases we shall neglect the possibility of the capture of electrons or holes by any electron-donating or electron-accepting centres. All the excess valence electrons are then present in the conductivity band and the missing electrons (holes) are in the valence band, DCS being defined as the difference between the volume concentrations of the conductivity electrons and holes:

$$N_e = n - p \cdot \qquad (16)$$

The activities of conductivity electrons and holes, $a_n$ and $a_p$, are linked by the following equation according to the Law of Mass Action:

$$\ln a_n + \ln a_p = 2 \ln K_i , \qquad (17)$$

which corresponds to the intrinsic ionisation reaction of the crystal, $K_i$ being the reaction equilibrium constant. On differentiating Eqns.(16) and (17) with respect to $N_e$ and on substituting the derivatives $dn/dN_e$ and $dp/dN_e$ in Eqn.(8) taking into account the definition of the thermodynamic factors for conductivity electrons $F_n = d\ln a_n/d\ln n$ and the analogous expression for holes, we find

$$\tilde{D}_e = \frac{nD_n + pD_p}{n/F_n + p/F_p} \cdot \qquad (18)$$

Hence it is seen that, when one type of electron carrier predominates, the CDC for electrons ($\tilde{D}_e$) is identical with the ICDC for these carriers, i.e. with $\tilde{D}_n$ for $n/F_n \gg p/F_p$ and with $D_p$ for $p/F_p \gg n/F_n$.

The dependence of $\tilde{D}_e$ on the degree of DCS in the region of comparable concentrations of electrons and holes can be readily determined by assuming that in this region the

†In the second of Wagner's communications[7] where the concentrations were expressed in equivalents per unit volume, the coefficient $z_1$ was omitted in the denominator of Eqn.(23c).

electrons are non-degenerate as a consequence of the smallness of $n$ and $p$. Eqn.(17) then assumes the simple form

$$np = K_i^2 \tag{19}$$

corresponding to the Boltzmann statistics and the solution of Eqns.(16) and (19) with subsequent substitution in Eqn.(8) yields the following results:

$$D_e = {}^1/_2 [\tilde{D}_n + \tilde{D}_p + (\tilde{D}_n - \tilde{D}_p) N_e (N_e^2 + 4K_i^2)^{-1/2}] \cdot \tag{20}$$

The parameters, $D_n$, $D_p$, $F_n$, and $F_p$ for electrons and holes are determined from the electrophysical properties of the crystal. Thus the random diffusion coefficient of conductivity electrons is linked to their mobilities $u_n$ by the Einstein relation $eD_n = kTu_n$, while the thermodynamic factor is equal to the ratio of the Fermi–Dirac integrals whose orders are 1/2 and −1/2:[12]

$$F_n = \frac{\Phi_{1/2}(\eta)}{\Phi_{-1/2}(\eta)}; \quad \Phi_j(\eta) = \frac{1}{j!}\int_0^\infty \frac{x^j\,dx}{\exp(x-\eta)+1} \quad , \tag{21}$$

where

$$\eta = (\mu_n - E_c)/kT$$

is the reduced Fermi energy and $E_C$ the energy of the bottom of the conductivity band. Analogous relations hold also for holes.

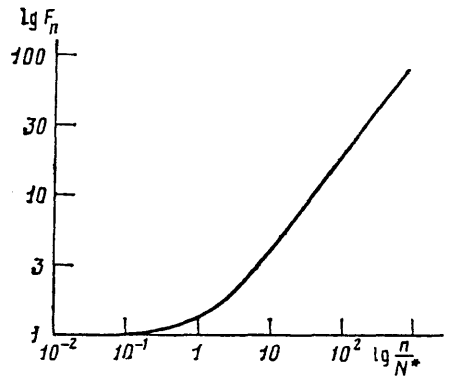



**Figure 1.** Dependence of the thermodynamic factor for conductivity electrons on their concentration.

Since $\Phi_{1/2}(\eta)$ is equal to the ratio of the concentrations of the electronic defects ($n$ or $p$) to the effective density of states in the corresponding band $N^* = 2(2\pi m^* kT)^{3/2}h^{-3}$ (where $m^*$ is the effective mass of the electron in the conductivity band and $h$ the Planck constant), Eqn.(21) makes it possible to calculate directly the thermodynamic factor $F_n$ (or $F_p$) as a function of the relative concentration of carriers $n/N^*$ or $p/N^*$. The result of this calculation, carried out with the aid of tables of Fermi–Dirac integrals,[13] is presented in Fig.1 for conductivity electrons; the result is analogous for holes. As can be seen from this plot, the electron gas can be regarded as virtually non-degenerate for $n < 0.1\,N^*$, where $F_n \cong 1$. When the degeneracy is marked, i.e. $n > 10\,N^*$, the thermodynamic factor can be defined to a satisfactory approximation by the formula

$$F_n = (\pi/6)^{1/3}(n/N^*)^{2/3}.$$

We shall establish several further useful relations between the electronic conductivity, the thermodynamic factors, and the CCD of electrons. We introduce an auxiliary quantity—the average macroscopic diffusion coefficient of electron carriers:

$$D_e = \frac{nD_n + pD_p}{n+p} = \frac{kT\sigma}{e^2(n+p)} \tag{22}$$

and define an effective thermodynamic factor for electrons with the aid of the relation $\tilde{D}_e = F_e D_e$. Comparison of the last equation with Eqn.(18) yields the expression

$$F_e = \frac{n+p}{n/F_n + p/F_p} \cdot \tag{23}$$

Hence it is seen that the quantity $F_e$ is unity in the absence of degeneracy and is equal to $F_n$ or $F_p$ when degeneracy obtains (for $n/F_n \gg p/F_p$ and $p/F_p \gg n/F_n$ respectively). Expressing $D_e$ in terms of $\tilde{D}_e$ in Eqn.(22), we obtain

$$\sigma = \frac{e^2(n+p)\tilde{D}_e}{kTF_e} \cdot \tag{24}$$

## 1. Structural Disorder

More than 300 solid-phase compounds belonging to a comparatively new class of crystal structures with properties which until recently appeared to be unique have now been synthesised. Their distinctive feature is the structural disorder of one of the components (silver, copper, or alkali metal cations and in certain alkaline earth metal or lanthanide halides at high temperatures, also the halide anions), statistically distributed among a large number of sites, several times greater than the number of ions.[1,14–18] As a result, the disordered component resembles an ionic liquid, i.e. its transport properties are similar to those of solutions or fused electrolytes. The electrical conductivity of these compounds is $10^{-2}$ – $10^{-1}$ $\Omega^{-1}$ cm$^{-1}$ even at room temperature, and, as a consequence of the high degree of disorder of the sublattice of only one of the components, the electrical conductivity of the crystal is unipolar. In the best solid electrolytes with structural disorder, also referred to as superionic conductors, the electronic component of the conductivity is negligible.[19,20] At the same time there exist a number of structurally disordered compounds which possess, together with the ionic component, also a considerable electronic component of the conductivity due to the deviations of their composition from stoichiometry.[21,22]

As a consequence of the unipolar ionic conductivity of structurally disordered phases, the effective CDC of the ions in them is identical with the ICDC of the disordered $k$ component. On the other hand, the latter is independent of the concentration of any species according to the theory of diffusion in solids[2] (p.243) and is defined by the expression

$$\tilde{D}_i = \tilde{D}_k = \frac{D_k}{[V_k]} = \nu r_0^2 \exp\left(-\frac{U_k}{kT}\right) , \tag{25}$$

where $[V_k]$ is the fraction of vacant sites in the $k$ sublattice, $\nu$ the vibration frequency of the ions, $r_0$ the length of the elementary jump, and $U_k$ the height of the potential barrier separating neighbouring sites.#

#It is easy to demonstrate that Eqn.(25) remains valid also when, as a consequence of the closeness of the allowed sites, each ion blocks $s > 1$ sites, so that the fraction of vacant sites is $1 - sN_k/N_L$, where $N_L$ is the total number of allowed sites.

Eqn.(25) reflects the following significant factor: if the $k$ sublattice contains ions of one kind only and vacancies, then the ICDC of these ions is the same as in systems with an unlimited free volume, i.e. with $[V_k] \to 1$, which are described by Einstein's diffusion theory. This result is important; it shows that an increase in the chemical diffusion coefficient owing to the increase in the thermodynamic factor occurs only for the upper limit of the quantities defined by Eqn.(25), specified by Einstein's theory.

We shall now proceed to the discussion of the CCDC of ions and electrons defined by the phenomenological Eqn.(7). Using Eqns.(3) and (25), we shall express the ionic conductivity in terms of the CDC of the ions: $kT\varkappa = q^2_k N_k \cdot [V_k]\tilde{D}_i$. Taking into account also Eqn.(24), we find from Eqn.(7) for $[V_k] \cong 1$

$$\tilde{D} = \frac{z_k^2 N_k F_e + (n+p)}{z_k^2 N_k F_e \tilde{D}_i + (n+p)\tilde{D}_e} \tilde{D}_i \tilde{D}_e \quad . \tag{26}$$

For not unduly large DCS, where $n + p \ll N_k$, the second term in the numerator in Eqn.(26) may be neglected. This is equivalent to the neglect of the second term of the phenomenological Eqn.(7), which is now formulated in a simplified form:

$$\tilde{D} = t_i \tilde{D}_e \quad . \tag{27}$$

We obtained Eqns.(26) and (27) for a crystal containing in the structurally disordered sublattice ions of only one kind $k$. It is easy to demonstrate that the above estimate of the second term in Eqn.(7) is at least qualitatively valid also for solid solutions containing ions of two or more kinds in the disordered sublattice.[23] In this case $t_i$ in Eqn.(27) should be understood as the total transport number of the ions.

The smallness of the second term in Eqn.(7) compared with the first has a definite physical basis associated with the high concentration of vacant sites $N_V$ in structurally disordered crystals. Since $N_V \cong N_k \gg |N_e|$, in most cases the relative changes in the concentrations of both ions and vacant sites actually attained remain negligibly small compared with the relative changes in the concentrations of electrons. By virtue of this relation, the intrinsic diffusional flux of ions in structurally disordered compounds is negligible and ions move virtually only under the influence of the internal electric field, which is directed in such a way that it diminishes the electron flux to a fraction $t_i$ of their intrinsic diffusional flux.

Since the mobilities and hence also the diffusion coefficients of the conductivity electrons and holes in solids are usually of the same order of magnitude, the dependence of $\tilde{D}_e$ on the degree of non-stoichiometry (Fig.1) is comparatively weak. For this reason, according to Eqn.(27), the character of the dependence of $\tilde{D}$ on $N_e$ is determined mainly by the change in the transport number of the ions. The corresponding curves have a maximum near the stoichiometric composition (for $D_n = D_p$ when the composition is exactly stoichiometric) and descend monotonically on either side of the maximum.

## 2. Fully Ionised Point Defects

We shall now consider a binary ionic crystal in which pair combinations of ionic point defects predominate for the stoichiometric composition: the Frenkel and Schottky defects or impurity atoms with effective charges corresponding to their complete ionisation. In this case the effective charges for the defects are determined by the valences of the corresponding components and amount to[1,2,24] $+z_1 e$ and $-z_2 e$ for the interstitial cations and anions, $-z_1 e$ and $+z_2 e$ for the cationic and ionic vacancies, and $\Delta q_f = q_f - q_k$ for the impurity centres formed by the substitution of the $k$ ion by an impurity ion $f$. Classical examples of crystals with impurity disorder are provided by the solid solutions AgCl + $CdCl_2$ ($\Delta q_f = +e$, compensating defects—cationic vacancies), $ZrO_2$ + CaO ($\Delta q_f = -2e$), and $ZrO_2$ + $Y_2O_3$ ($\Delta q_f = -e$, compensating defects—anionic vacancies).

In the general case the ionic conductivity of a binary compound, both pure and in the presence of impurities, can be determined by the interstitial cations and anions and also by the cationic and anionic vacancies. For this reason, the ionic conductivity of the $k$ component is expressed, according to the Nernst–Einstein relation, in terms of the diffusion coefficients of these defects:

$$kT\varkappa_k = q_k^2 (N_{ki} D_{ki} + N_{Vk} D_{Vk}) , \tag{28}$$

where the subscripts $ki$ and $Vk$ refer to the interstitial ions $k$ and the vacancies in the $k$ sublattice. According to the microscopic model of the transport of defects, their diffusion coefficients are determined by expressions of the type of Eqn.(25): $D = \nu r_0^2 \exp(-U/kT)$ and, in terms of the approximation of non-interacting defects, are independent of their concentrations and hence also of the DCS. On the other hand, within the framework of the phenomenological description of diffusion, the ionic conductivity of a binary compound is expressed in terms of the macroscopic diffusion coefficients of ions

$$D_k, \quad kT\varkappa_k = q_k^2 N_k D_k .$$

Comparison of this relation with Eqn.(28) leads to the familiar expression for $D_k$ in terms of the microscopic characteristics of the system:

$$N_k D_k = N_{ki} D_{ki} + N_{Vk} D_{Vk} , \tag{29}$$

Furthermore, if there is a local equilibrium between ionic point defects in the crystal, then their concentrations are related by the expressions for the chemical potentials of the ions (at no unduly high concentrations):

$$\mu_k = \mu_{ki}^0 + kT \ln N_{ki} = -\mu_{Vk}^0 - kT \ln N_{Vk} , \tag{30}$$

where $\mu^0_{ki}$ and $\mu^0_{Vk}$ are the standard chemical potentials of the ions and vacancies in the $k$ sublattice. By virtue of the Gibbs–Duhem relation, the following equation is then valid:

$$z_1 \mu_1 + z_1 \mu_2 = 0 . \tag{31}$$

In addition, the concentrations of the defects are linked by the electroneutrality condition for the crystal:

$$N_e = z_1 (N_{MI} - N_{VM}) + z_2 (N_{VX} - N_{XI}) + (\Delta q_f / e) N_f , \tag{32}$$

where $N_f$ is the constant volume concentration of the impurity ions.

On differentiating Eqns.(30) and (32) with respect to $N_e$ and on substituting the derivatives in Eqn.(8), taking into account Eqn.(29), we obtain the expression for the average CDC for the ions:

$$\tilde{D}_i = \frac{z_1^2 (N_{MI} D_{MI} + N_{VM} D_{VM}) + z_2^2 (N_{XI} D_{XI} + N_{VX} D_{VX})}{z_1^2 (N_{MI} + N_{VM}) + z_2^2 (N_{XI} + N_{VX})} \quad . \tag{33}$$

Here the summation has been carried out over the principal cations and anions and the contribution of the impurity ions to the transport was assumed to be negligible.

The exact dependence of $\tilde{D}_i$ on the DCS can be obtained by solving simultaneously for the concentration of the defects one of the equations of the Law of Mass Action [Eqns.(30) and (31)], which corresponds to a dominant disorder, and the simplified equation for the electroneutrality condition [Eqn.(32)]. It is readily seen that in the case of intrinsic

ionic defects (Frenkel or Schottky) the solutions are analogous to Eqn.(20) for the CDC for electrons in the absence of degeneracy and the corresponding plots of $\tilde{D}_i$ against $N_e$ are similar to those in Fig.1. In particular, for high DCS, where one kind of ionic defect predominates, the $\tilde{D}_i$ curves approach asymptotically the diffusion coefficient of the given defect: $D^i_{Mi}$ or $D_{VX}$ in the presence of an excess of the metal and $D_{Xi}$ or $D_{VX}$ in the presence of an excess of the non-metal.

In the case of the impurity disorder, the excess charge of the impurity is compensated by one specific kind of intrinsic ionic defect. For this reason, according to Eqn.(8), $\tilde{D}_i$ is identical with the ICDC of the corresponding ions $\tilde{D}_k$ and, according to Eqn.(33), has a constant value equal to the diffusion coefficient of the compensating defect ($D_{ki}$ or $D_{Vk}$) over a wide range of $N_e$.

Comparison of the results with Eqn.(29) shows that, in transport by point defects, the CDC for the ions exceed appreciably, usually by several orders of magnitude, the corresponding values of their macroscopic diffusion (self-diffusion) coefficients. The accelerating effect of thermodynamic factors, which increase $\tilde{D}$ up to the Einstein values $D_{ki}$ or $D_{Vk}$, is in this case manifested even more distinctly than in the case of structural disorder.

On comparing Eqns.(28) and (33), we also obtain a relation between the ionic conductivity of the binary crystal and the CDC for the ions:

$$kT\varkappa = e^2 [z_1^2 (N_{Mi} + N_{VM}) + z_2^2 (N_{Xi} + N_{VX})] \tilde{D}_i \quad . \qquad (34)$$

Together with Eqn.(24), this relation makes it possible to express the transport numbers of the ions and electrons in terms of the corresponding CDC and to determine the CCDC for the ions and electrons in accordance with Eqn.(7):

$$\tilde{D} = \frac{[z_1^2 (N_{Mi} + N_{VM}) + z_2^2 (N_{Xi} + N_{VX})] F_e + (n+p)}{[z_1^2 (N_{Mi} + N_{VM}) + z_2^2 (N_{Xi} + N_{VX})] F_e \tilde{D}_i + (n+p) \tilde{D}_e} \tilde{D}_i \tilde{D}_e \quad . \qquad (35)$$

The instances of not unduly high DCS, where the term $n + p$ in the numerator in Eqn.(35) can be neglected compared with the concentrations of the ionic defects, are of special interest. The solutions thus obtained will be analysed in detail in the next Section; here it is sufficient to note that the above simplification is equivalent to the formulation of the phenomenological Eqn.(7) in the abbreviated form (27). The physical significance of this simplification is the same as in the case of structural disorder: the gradients of the chemical potentials of the ions are negligible compared with those for electrons and ions move virtually only under the influence of the electric fields.

## IV. COUPLED CHEMICAL DIFFUSION COEFFICIENTS OF IONS AND ELECTRONS IN CRYSTALS WITH DIFFERENT DEFECT STRUCTURES

### 1. The Wagner Disorder. Neutral Defects

We shall refer to the Wagner disorder by the term combined ionic-electronic disorder in which the electroneutrality condition assumes one of the following simplified forms:

$$n = \zeta N^{\zeta+}_{Mi}; \; n = \zeta N^{\zeta+}_{VX}; \; p = \zeta N^{\zeta-}_{Xi}; \; p = \zeta N^{\zeta-}_{VM} \quad . \qquad (36)$$

Here the effective charge on the dominant ionic defect $\zeta$ can assume any integral value ranging from unity to one equal to the valence of the corresponding component $z_k$. The special case of the Wagner disorder, corresponding to the total ionisation of the defects ($\zeta = z_k$) satisfies the formal treatment developed in the previous Section and can be described with the aid of Eqn.(35). We shall discuss below the cases of an arbitrary degree of ionisation of defects ($\zeta \leq z_k$), including the case of dominant neutral defects.§

We shall now re-examine the binary compound $MX_r$; we shall assume that in the most general case it contains interstitial cations and anions as well as cationic and anionic vacancies with arbitrary integral effective charges $\zeta$ ranging from zero (neutral defects) to $z_k$ (fully ionised defects). Assuming that the concentration of the impurity is negligibly small, we can formulate the electroneutrality condition in the following form:

$$N_e = z_1 \sum_{\zeta=0}^{z_1} (N^{\zeta+}_{Mi} - N^{\zeta-}_{VM}) + z_2 \sum_{\zeta=0}^{z_2} (N^{\zeta+}_{VX} - N^{\zeta-}_{Xi}) \quad . \qquad (37)$$

In conformity with the last equation, the overall flux of electrons in excess of the stoichiometric composition is described by the expression

$$J_e = z_1 \sum_{\zeta=0}^{z_1} (J^{\zeta+}_{Mi} - J^{\zeta-}_{VM}) - z_2 \sum_{\zeta=0}^{z_2} (J^{\zeta-}_{Xi} - J^{\zeta+}_{VX}) \quad . \qquad (38)$$

According to the Wagner equation [Eqn.(2)], the fluxes of defects are proportional to the gradients of their electrochemical potentials, the electrochemical potentials of the defects being linked to the chemical potentials of the atoms and electrons by the obvious relations

$$\begin{aligned} \mu^{\zeta+}_{Mi} &= \mu_M - \zeta\mu_e; \; \mu^{\zeta-}_{VM} = -\mu_M + \zeta\mu_e; \\ \mu^{\zeta-}_{Xi} &= \mu_X + \zeta\mu_e; \; \mu^{\zeta+}_{VX} = -\mu_X - \zeta\mu_e \quad . \end{aligned} \qquad (39)$$

Furthermore, in the case of the Wagner disorder, the concentrations of the electron and ion carriers in the crystals are comparable according to Eqn.(36). On the other hand, since the mobility of the conductivity electrons and holes as a rule exceeds by several orders of magnitude the mobility of the interstitial ions and vacancies, such crystals always have a predominantly electronic conductivity. On this basis, we put $\sigma \gg \varkappa$. The electric field gradient $\nabla\phi$ is then determined from the condition that the electrochemical potential of the electron is constant ($\nabla\phi = \Delta\mu_e/e$) and we obtain from Eqn.(38)

$$\begin{aligned} kTJ_e = -\Bigg[ & z_1 \sum_{\zeta=0}^{z_1} (N^{\zeta+}_{Mi} D^{\zeta+}_{Mi} + N^{\zeta-}_{VM} D^{\zeta-}_{VM}) \frac{d\mu_M}{dN_e} - \\ & - z_2 \sum_{\zeta=0}^{z_2} (N^{\zeta-}_{Xi} D^{\zeta-}_{Xi} + N^{\zeta+}_{VX} D^{\zeta+}_{VX}) \frac{d\mu_X}{dN_e} \Bigg] \Delta N_e \quad . \end{aligned} \qquad (40)$$

The coefficient of $\nabla N_e$ is the CCDC for the ions and electrons $\tilde{D}$ multiplied by $kT$. Taking into account the Gibbs–Duhem relation in the form

$$d\mu_M = -\frac{z_1}{z_2} d\mu_X = -\frac{z_1 kT}{2z_2} d\ln p_{X_2} \quad , \qquad (41)$$

where $p_{X_2}$ is the partial pressure of the non-metal in the surrounding medium, we obtain the following expression for $\tilde{D}$:

$$\begin{aligned} \tilde{D} = -\Bigg[ & z_1^2 \sum_{\zeta=0}^{z_1} (N^{\zeta+}_{Mi} D^{\zeta+}_{Mi} + N^{\zeta-}_{VM} D^{\zeta-}_{VM}) + \\ & + z_2^2 \sum_{\zeta=0}^{z_2} (N^{\zeta-}_{Xi} D^{\zeta-}_{Xi} + N^{\zeta+}_{VX} D^{\zeta+}_{VX}) \Bigg] \frac{1}{2z_2} \frac{d\ln p_{X_2}}{dN_e} \quad . \end{aligned} \qquad (42)$$

§ Although the diffusion of neutral defects is not associated with the separate movement of electrons, the formal treatment employed here remains valid also for such diffusion, provided that we put $q_k = 0$ in the Wagner equation [Eqn.(2)].

Eqn.(42) is a generalisation of the formula obtained[26] for bivalent metal oxides with the Wagner disorder involving interstitial cations or cationic vacancies with arbitrary degrees of ionisation.

The reciprocal of the derivative in Eqn.(42) will be expressed in the following form taking into account Eqn.(37):

$$\frac{d N_e}{d \ln p_{X_2}} = z_1 \sum_{\zeta=0}^{z_1} \left( N_{Mi}^{\zeta+} \frac{d \ln N_{Mi}^{\zeta+}}{d \ln p_{X_2}} - N_{VM}^{\zeta-} \frac{d \ln N_{VM}^{\zeta-}}{d \ln p_{X_2}} \right) + + z_2 \sum_{\zeta=0}^{z_2} \left( N_{VX}^{\zeta+} \frac{d \ln N_{VX}^{\zeta+}}{d \ln p_{X_2}} - N_{Xi}^{\zeta-} \frac{d \ln N_{Xi}^{\zeta-}}{d \ln p_{X_2}} \right) .$$

Under the conditions of the Wagner disorder, the concentrations of all the defects are power functions of the partial pressure of the non-metallic component $X_2$: the quantities $N_{VM}$ and $N_{Xi}$ are proportional to $p_{X_2}^{1/m}$, while $N_{Mi}$ and $N_{VX}$ are proportional to $p_{X_2}^{-1/m}$. The values of the parameter $m$ can be readily calculated by the Kroger–Wink method[27] for a specified simplified form of the electroneutrality condition and those for the dominant defects can be obtained by direct experimental determination.[28] Taking into account this relation, we obtain finally

$$\tilde{D} = \frac{z_1^2 \sum_{\zeta=0}^{z_1} (N_{Mi}^{\zeta+} D_{Mi}^{\zeta+} + N_{VM}^{\zeta-} D_{VM}^{\zeta-}) + z_2^2 \sum_{\zeta=0}^{z_2} (N_{Xi}^{\zeta-} D_{Xi}^{\zeta-} + N_{VX}^{\zeta+} D_{VX}^{\zeta+})}{2 z_1 z_2 \sum_{\zeta=0}^{z_1} (N_{Mi}^{\zeta+}/m_{Mi}^{\zeta+} + N_{VM}^{\zeta-}/m_{VM}^{\zeta-}) + 2 z_2^2 \sum_{\zeta=0}^{z_2} (N_{Xi}^{\zeta-}/m_{Xi}^{\zeta-} + N_{VX}^{\zeta+}/m_{VX}^{\zeta+})} . \quad (43)$$

A special case of this formula was obtained in our earlier study in connection with the description of the coupled diffusion of oxygen ions and electrons in vanadium oxide compounds.[29]

## 2. Electronic Disorder

When electronic disorder of the intrinsic type is dominant, the concentrations of electrons and holes are equal and identical with the ionisation constant $K_i$ – $n \cong p \cong k_i$. When disorder of the impurity type predominates, the concentration of electrons is equal to the concentration of donors $N_d - n \cong N_d^+$ or the concentration of holes is equal to the concentration of acceptors $N_A - p = N_A$. The concentrations of defects in these formulae can be calculated for each specific type of disorder predominating under the conditions of the stoichiometric composition. The corresponding expressions for the CCDC, which are valid over a wide range of concentrations of defects, include only the deviation from the stoichiometric composition $N_e$ and also some of the equilibrium constants (the intrinsic ionisation constant $K_i$ and the defect formation constants $K_F$ for the Frenkel defects, $K_{AF}$ for the anti-Frenkel defects, and $K_S$ for the Schottky defects) or the impurity concentration $N_f$. As an example one may point to a study[30] in which the CCDC for ions and electrons in a uni-univalent ionic crystal with Schottky defects and dominant electronic conductivity, corresponding to a non-degenerate state, was calculated.

We shall not formulate here the exact expressions for $\tilde{D} = \tilde{D}(N_e)$ in view of their cumbersome nature and we shall confine ourselves to the analysis of simplified solutions to which the above expressions reduce in certain limiting cases of interest for practical application. All these expressions can be divided into two groups depending on the dominant type of conductivity in the crystal.

(a) *Case where the ionic conductivity is dominant* ($\varkappa \gg \sigma$, $t_i \cong 1$). This case obtains in solid electrolytes within the electrolytic region[1] where the DCS are comparatively small and the concentrations of the electronic carriers ($n + p$) can be neglected in Eqns.(26) and (35) compared with the concentrations of the ionic carriers. For both structurally disordered compounds and for crystals with point defects, intrinsic or impurity, the relation $\tilde{D} \cong \tilde{D}_e$ follows from Eqn.(27) under these conditions. From the standpoint of physics, this implies that the electrons move solely under the influence of the gradient of the chemical potential; on the other hand, ions have virtually constant chemical potentials and move solely under the influence of the electric field.

This result is analogous to that well known in the electrochemistry of solutions for the diffusion of charged species present at low concentration in the supporting electrolyte.[7,31] In the present case, such species are conductivity electrons or holes and the disordered ions form a conducting background, which fully screens off the influence of the electric field. This factor is widely used in the study of electron transport in solid electrolytes, in particular in the experimental determination of the mobilities of electrons and holes.[20,32,33]

(b) *Case where the electronic conductivity is dominant* ($\sigma \gg \varkappa$ ; $t_e \cong 1$). We shall consider initially crystals with structural disorder and with fully ionised point defects for not unduly high DCS where one can neglect the term $n + p$ in the numerators of Eqns.(26) and (35) and the first terms incorporating $\tilde{D}_i$ in their denominators by virtue of the condition $\sigma \gg \varkappa$. Further simplifications are possible in the following limiting cases.

I. Small DCS. For compositions close to the stoichiometric, where $|N_e| \ll K_i$, the concentrations of conductivity electrons and holes are approximately the same and equal to the intrinsic ionisation constant $K_i$; the electron–hole gas is non-degenerate. The concentrations of the ionic carriers in this region are also approximately constant and are determined either by the crystallography of the compound (structural disorder), or by the formation constants of the dominant ionic defects $K_F$, $K_{AF}$, and $K_S$ (intrinsic ionic disorder), or by the content of the heterovalent impurity $N_f$ (impurity ionic disorder).

In the case of structural disorder, Eqn.(26) for the CCDC is simplified to the expression

$$\tilde{D}_k = \frac{z_k^2 N_k}{2K_i} D_k . \quad (44)$$

Simplified expressions can be obtained from Eqn.(35) for various types of dominant point defects. Having used Eqn.(29) to replace the microscopic diffusion coefficients $D_{ki}$ and $D_{Vk}$ in these expressions by the macroscopic coefficients $D_k$ for all types of dominant ionic disorder, both structural and point disorder, we obtain a single formula for small DCS:

$$\tilde{D} = \frac{z_1^2 N_1 D_1 + z_2^2 N_2 D_2}{2K_i} . \quad (45)$$

II. Intermediate DCS. This includes very high degrees of DCS where $|N_e|$ is large compared with the intrinsic ionisation constant $K_i$ but small compared with the characteristic concentration of the disordered ions ($N_k$ for structural disorder and the largest of the quantities $K_F$, $K_{AF}$, $K_S$, or $N_f$ in the case of fully ionised point defects). In this region the electronic carriers consist virtually of conductivity electrons only or holes only, so that their total concentration is specified by the DCS: $n + p \cong |N_e|$. On the other hand, the concentrations of the ionic defects are the same as in the previous case. Simplified solutions for the CCDC taking into account Eqn.(29) can be represented

in a single form expressing $\tilde{D}$ in terms of the macroscopic diffusion coefficients of the ions:

$$\tilde{D} = \frac{F_e}{|\delta|}(z_1 D_1 + z_2 D_2) \ . \qquad (46)$$

The relative DCS is in this case designated by $\delta$: $\delta = N_e/z_1 N_1 = N_e/z_2 N_2$. In the absence of degeneracy of electrons, $F_e = 1$ and Eqn.(46) becomes identical with the familiar Wagner formula.[7]

Together with the two approximations considered, Eqn.(35) permits yet another approximation corresponding to the Wagner disorder under the conditions of the total ionisation of the defects. The solution for this situation constitutes a special case of the solutions examined below.

III. Large DCS. In this range of DCS the relation $|N_e| \cong n + p$ is retained and in addition the quantity $|N_e|$ exceeds the concentration of the ionic point defects characteristic of the stoichiometric composition, i.e. the largest of the constants $K_F$, $K_{AF}$, $K_S$, or $N_f$. This case corresponds to either the Wagner disorder, characterised by one of the electroneutrality conditions [Eqn.(36)], or the neutral defects $K_i^{\times}$ of $V_k^{\times}$ (an effective zero charge has come to be designated by the oblique cross $\times$). In both cases the DCS is determined by Eqn.(37). Simplified expressions for the CCDC follow directly from Eqn.(43), provided that one term, corresponding to the dominant defect, is left in its numerator and denominator.

The parameter $m$ for the dominant defects can be readily calculated, taking into account the possible degeneracy of electrons, by differentiating Eqn.(39) with respect to $\ln p_{X_2}$, having first transformed $d\mu_e$ with the aid of the relation $d \ln a_e = F_n d \ln n = -F_p d \ln p$ and taking into account Eqns.(36) and (41). Then one obtains the values of $m_1 = 2z_2(\zeta F_e + 1)/z_1$ for the dominant cationic defects $M_i^{\zeta+}$ or $V_M^{\zeta-}$ and $m_2 = 2(\zeta F_e + 1)$ for the anionic defects $X_i^{\zeta-}$ or $V_X^{\zeta+}$— both charged and neutral. In both cases Eqn.(43) reduces to simple expressions, namely under the conditions of the Schottky disorder to

$$\tilde{D}_k = (\zeta F_e + 1) D_{ki}$$

and in the case of the impurity vacancy disorder to

$$\tilde{D}_k = (\zeta F_e + 1) D_{Vk} \ .$$

When Eqn.(29) is taken into account, the above solutions reduce to the general formula

$$\tilde{D} = \frac{\zeta F_e + 1}{|\delta|} D_k \qquad (47)$$

For $F_e = 1$, this formula was obtained by Childs and Wagner.[34] The unity added to the numerator (47) compared with Eqn.(46) is due to the fact that in this case the ions move not only under the influence of the electric field but also as a result of the gradient of their chemical potential, which is related to the variable concentration of defects.

Despite the formal similarity of Eqns.(46) and (47), they determine significantly different dependences of $\tilde{D}$ on the degree of DCS $\delta$. Thus, when $F_e = 1$, the coefficient $D_k$ in region II is constant and, according to Eqn.(46), $\tilde{D}$ is inversely proportional to $|\delta|$; in region III the quantity $D_k$ is directly proportional to $|\delta|$ and, according to Eqn.(47), $\tilde{D}$ is constant.

The qualitative form of the dependence of $\lg \tilde{D}$ on $\delta$ is represented in Fig.2 for a crystal with fully ionised Schottky defects, which are converted into Wagner defects for high values of $|\delta|$ when $K_S \gg K_i$ and $D_{VM} > D_{VX}$. The maximum value of $\lg \tilde{D}$ is attained for the stoichiometric composition. The characteristic values of $\delta = \pm K_S/N_k$, for which solution II [Eqn.(46)] is converted into solution III [Eqn.(47)], are shown on the abscissa axis. For crystals with Frenkel defects, analogous relations are obtained; for the structural disorder, the difference consists in the fact that the simplified solution III is not obtained and the horizontal sections on the plots of $\lg \tilde{D}$ against $\delta$ are not attained even for the maximum value of $|\delta|$.

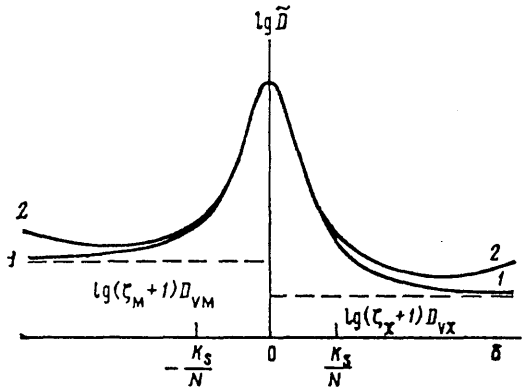



**Figure 2.** Dependence of the coupled diffusion coefficient $\tilde{D}$ on the degree of non-stoichiometry of a crystal with Schottky defects in the absence (curve *1*) and presence (curve *2*) of degeneracy of the electrons.

When electronic disorder is dominant, Eqn.(44) also simplifies markedly, but only one term corresponding to atomic defects with the maximum concentration is left in its numerator and denominator. One then obtains $\tilde{D} \cong D_{def}$— a result which is formally identical with solution II for the case where neutral defects with $\zeta = 0$ predominate. Such agreement is entirely understandable, because under conditions where the electronic disorder predominates the gradient of the chemical potential of the electrons is negligible. Under the conditions of electronic equilibrium, this also leads to a low electric field strength, since the ionic defects move only under the influence of the intrinsic chemical potential gradient.

An especially important feature of the results obtained is very high values of CCDC compared with the self-diffusion coefficients of the ions. Indeed, even for high degrees of DCS, the coefficients $\tilde{D}$ are of the same order of magnitude as the diffusion coefficient of the dominant ionic defects and, as the stoichiometric composition is approached, they increase still further in inverse proportion to $|\delta|$ in the region of moderate DCS (region II).

The large number of limiting solutions for the CCDC greatly hinders the interpretation of the experimental data even as regards fundamental characteristics such as the effective activation energy. For crystals with ionic point defects, this quantity has the simple significance of the height of the potential barrier $U$ to ion jumps only in region III. Since the values of $\tilde{D}$ in region I can vary as a function of the transport numbers of the ions from $\tilde{D}_e$ for $t_i \cong 1$ to $z_k^2 N_k D_k / 2K_i$ for $t_i \ll 1$, in this region the effective activation energy has indefinite values or totally loses its significance.

Thus, according to Weppner,[36] $\tilde{D}$ in the β-modification of silver sulphide increases with temperature in accordance with the usual exponential law only in the region of fairly high values of $\delta$; for the stoichiometric composition, this relation is reversed partly owing to the decrease of the mobility of the electron carriers with temperature.

## V. EXPERIMENTAL DETERMINATION OF CHEMICAL DIFFUSION COEFFICIENTS

### 1. Theoretical Principles

The majority of the methods for the experimental determination of chemical diffusion coefficients in solids used nowadays are based on the study of the relaxation of the concentration profile in the diffusion medium under the influence of some kind of external perturbation—an abrupt change in potential, current, or composition of the ambient atmosphere.[6,34] The problem is as a rule reduced to the solution, subject to appropriate initial and boundary conditions, of the phenomenological equation of Fick's Second Law:

$$\frac{\partial N}{\partial t} = \tilde{D}\,\mathrm{div}\,\nabla N \equiv \tilde{D}\nabla^2 N\,, \qquad (48)$$

where the effective CDC is assumed to be independent of the concentration in the experimental range. On the basis of the observed dependence of the concentration $N$ on the coordinate $x$ and the time $t$, the response of the system to the perturbation, i.e. the time variation of the measured quantity (current, potential, weight, or electrical conductivity of the specimen) is calculated. The effective CDC is found by comparing the theoretical and experimental results.

In the case of the coupled chemical diffusion considered in this review, the flux of electrons in a non-stoichiometric crystal is described by the expression

$$J_e = -\frac{t_e}{e} I - \tilde{D}\nabla N_e\,, \qquad (49)$$

where the first term corresponds to the contribution of these electrons to the electric current $I$ which has passed through the specimen. The material balance condition $\partial N_e/\partial t = -\mathrm{div}\,J_e$ converts Eqn.(49) into a differential equation, which is converted into Fick's Second Law [Eqn.(48)] for constant $t_e$ and $\tilde{D}$. Thus the principal approximation in the problem reduces to the assumption of a low degree of inhomogeneity of the diffusion medium, for which the relative change in $N_e$ or $\delta$ is small compared with unity (so that the kinetic parameters $\varkappa$, $\sigma$, $t_i$, $t_e$, and $\tilde{D}$ can be assumed constant). This requires in its turn the use in experiments of weak perturbations to stimulate the diffusion process.

Investigations during the last decade have shown that electrochemical methods using galvanic cells with solid electrolytes are most convenient and reliable.[6,37–41] We shall therefore concentrate attention on them in the present review.

In the electrochemical method the principal element of the measuring circuit is a cell of the following type:

| auxiliary electrode | solid electrolyte | test specimen | inert electrode. | (50) |
|---|---|---|---|---|

The solid electrolyte must exhibit unipolar ionic conductivity with respect to one of the ions forming part of the composition of the test compound, so that the electric current passing through the cell can serve as an exact measure of the change in the composition of the test specimen. The majority of the investigations have been carried out with $ZrO_2$, β-$Al_2O_3$, AgI, and CuBr specimens satisfying the above requirement over a fairly wide range of temperatures and compositions of the gaseous medium.[38–42] The auxiliary electrode, which is reversible with respect to the electrolyte, serves as a source of ions, which are supplied to the test specimen via the electrolyte, and also ensures the measurement of the chemical potential of the electrochemically active element at the electrolyte/specimen boundary.

### 2. Potentiostatic Method

In this method[6,38,40–46] the test specimen is first maintained under equilibrium conditions so that its composition becomes homogeneous throughout its thickness. Then, at a time $t = 0$, a potential $\Delta\phi$, different from the e.m.f. $E$ of the cell at equilibrium, is applied to this cell. The potential difference at the boundaries of the test specimen with a length $L$, given by $\phi|_{x=0} - \phi|_{x=L}$, where $\phi|_{x=0}$ is the potential at the electrolyte–specimen boundary and $\phi|_{x=L}$ the potential at the specimen–inert electrode boundary, amounts to $\Delta\phi - E$. This quantity must be sufficiently small so that it is possible to neglect the concentration dependence of the transport number $t_e$ and the diffusion coefficient $\tilde{D}$ and also the overpotential (the additional potential jump due to the slow charge transfer through the electrolyte/specimen interface and the ohmic losses in the electrolyte and the specimen). Furthermore, the cell must be constructed in such a way that there is no transport of ions through the lateral surfaces of the specimen and through its end surface opposite to the electrode. This is usually achieved by constructing the current lead at the right-hand end of cell (50) from an inert material (platinum, graphite) while the right-hand side of cell (50) is placed in an inert atmosphere. In subsequent calculations it is also assumed that the current, which during the short time interval after the application of the potential $\Delta\phi$ to the cell transports a certain amount of electricity consumed in altering the charge of the double layer at the interfaces, is likewise small.

Under these conditions at time $t = 0$, a concentration of excess electrons $N_\infty$, different from the initial concentration $N_0$ and corresponding to equilibrium in relation to the new potential, is established in the layer of specimen adjoining the electrolyte ($x = 0$). The subsequent relaxation process is effected by the coupled diffusion of ions and electrons through the specimen, as a result of which the concentration of electrons throughout the bulk of the specimen tends to the finite value $N_\infty$. Since this process involves a continuous supply of the corresponding amount of ions from the auxiliary electrode through the electrolyte, the electric current flowing through the cell is a measure of its rate. In its experimental aspect, the potentiostatic method therefore reduces to the measurement of the current as a function of time.

The current density in the cell is determined from the condition that there is no electron flux at the boundary between the specimen and the electrolyte. According to Eqn.(49), this gives rise to the boundary condition

$$t_e I = eD\nabla N_e \text{ when } x=0\,. \qquad (51)$$

At the specimen–inert electron boundary, the flux of ions is zero and the current passed through the system is wholly due to electrons ($I = -eJ_e$ and, in conformity with Eqn.(49), the second boundary condition is obtained in the form

$$t_i I = eD\nabla N_e \text{ when } x=L\,. \qquad (52a)$$

The authors of the above studies used the simpler boundary condition at $x = L$ in the form

$$\nabla N_e(L) = 0\,, \qquad (52b)$$

which is valid, as can be seen from Eqn.(52a), for small ionic transport numbers $t_1$.

In the subsequent exposition, we shall also confine ourselves to the boundary condition (52b), which is applicable to materials in which electronic conductivity predominates.

Thus, in the case of the one-dimensional diffusional problem, i.e. for plane-parallel boundaries of the specimen located at $x = 0$ and $x = L$, it is necessary to solve Fick's Second Law $\partial N/\partial t = \tilde{D}\partial^2 N/\partial x^2$ subject to the initial condition $N(x, 0) = N_0$ and the boundary conditions $N|_{x=0} = N_\infty$ and $(\partial N/\partial x)_{x=L} = 0$ (here and henceforth the subscript $e$ is omitted in the symbol $N$ denoting concentration).

The solution has the form[47,48]

$$N(x,t) = N_\infty + (N_0 - N_\infty)\,\psi(x,t)\,. \qquad (53)$$

The function

$$\psi(x,t) = \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{1}{2n+1}\sin\frac{(2n+1)\pi x}{2L}\exp\left[-\frac{(2n+1)^2\pi^2\tilde{D}t}{4L^2}\right] \qquad (54)$$

assumes the following limiting values: $\psi(0, 0) = 0$, $\psi(L, 0) = 1$, and $\psi(x, \infty) = 0$. Depending on $t$, this function can be synthesised in two limiting cases.

1. Short times ($t \gg L^2/\tilde{D}$). At the beginning of the process the effective length of the diffusion zone $2(Dt)^{1/2}$ is small compared with the length of the specimen $L$ and the diffusion can be described by the solution for a semi-infinite medium: $\psi(x, t) \cong \mathrm{erf}\,[x/2(Dt)^{1/2}]$. Hence, according to Eqn.(51), we obtain the following expression for $t_e \cong 1$:

$$I \cong e(N_\infty - N_0)(\tilde{D}/\pi t)^{1/2}\,. \qquad (55)$$

Consequently the CCDC can be determined from the slope of the experimental $I$–$t^{-1/2}$ line, provided that the difference between the final and initial concentrations $N_\infty - N_0$ is known. This difference can be expressed in terms of the total amount of electricity passed through the specimen before the attainment of equilibrium: $Q = Ve(N_\infty - N_0)$, where $V$ is the volume of the specimen. However, this method is associated with the integration of the current with respect to time and can lead to a major error as a consequence of the slow decay of the current in the range of its values close to the limit of the sensitivity of the measuring apparatus.

The coulometric titration method developed by Wagner[49–51] and used widely nowadays in research practice is much more convenient for the determination of the difference between the final and initial concentrations of electrons in the specimen $N_\infty - N_0$. In this method a cell of type (50), for example

$$\mathrm{M}\,\left|\begin{matrix}\text{electrolyte}\\ \mathrm{M}^{z+}\end{matrix}\right|\,\mathrm{M}_{1+\delta}\mathrm{X}_r\,\left|\,\mathrm{Pt}\right.\,. \qquad (56)$$

is also used. A definite amount of electricity is passed through the cell, after which it is allowed to stand for a time until the attainment of a homogeneous value of $\delta$ over the entire length of the specimen; for each fixed value of $\delta$, the cell e.m.f. $E$ is measured. The $E = E(\delta)$ curve plotted in this way is a calibration curve and is used to determine the unknown value of $\delta$ from the measured e.m.f. Furthermore, the e.m.f. of cell (56) is equal to $(\mu_M^0 - \mu_M)/ze$, where $\mu_M^0$ and $\mu_M$ are the chemical potentials of the atoms M in the metallic electrode and in the compound $\mathrm{M}_{1+\delta}\mathrm{X}_r$. Graphical differentiation of the $E(\delta)$ curve therefore makes it possible to determine directly the thermodynamic factor $F_M$:

$$F_M = \frac{d\ln a_M}{d\ln N_M} = -\frac{ze}{kT}\cdot\frac{dE}{d\delta}\,, \qquad (57)$$

which can be used to calculate $\tilde{D}$ from self-diffusion data in accordance with Eqn.(4).

2. Long times ($t > L^2/4\tilde{D}$). In this case Eqn.(54) for $\psi(x, t)$ is fitted by the first member of the series and we obtain the following expression for the current (to within <1%):

$$I \cong \frac{2e(N_\infty - N_0)}{L}\exp\left(-\frac{\pi^2\tilde{D}t}{4L^2}\right)\,. \qquad (58)$$

Eqn.(58) describes the $\ln|I| - t$ straight line. $\tilde{D}$ can be determined from its slope.

Using the potentiostatic method, Rickert and Weppner,[45] determined the CCDC in non-stoichiometric wustite $\mathrm{Fe}_{1-\delta}$ = 0 in the range $0.06 \leqslant \delta \leqslant 0.13$ using all the three methods described. The discrepancy between the data obtained by different procedures does not exceed 30%, indicating their adequate reliability.

Relations similar to those described above are also obtained for the cylindrical geometry of cell (48) in which the test substance is first fused within a solid electrolyte tube.[41] In this case the overall solution of Fick's second equation is expressed in terms of Bessel functions, but for short times it is identical with Eqn.(55).

### 3. The Galvanostatic Method

This method, which is fairly simple as regards apparatus, has been widely used by many investigators.[6,11,38–46,52,53] Its theory has been developed by Yokota[11] for compounds of the type of silver sulphide exhibiting cationic and electronic conductivities. However, his equations proved valid for any binary ionic compound and we shall therefore quote the general relations.

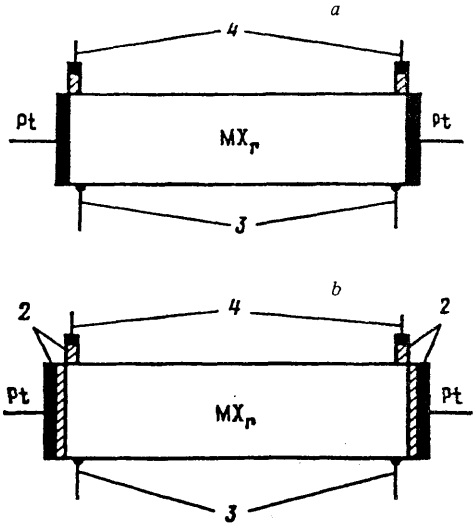



**Figure 3.** Cell with electronic (*a*) and ionic (*b*) electrodes for the determination of the CCDC by the galvanostatic method: 1) inert electrodes; 2) electrolyte; 3) electronic probes; 4) ionic probes.

We shall consider cells of two types, illustrated schematically in Fig.3. Cell *a* has electrodes made of platinum, graphite, or another inert material which is permeable to electrons only. Cell *b* is fitted with more complex electrodes, containing a layer of solid electrolyte impermeable to electrons and reversible with respect to the ions $M^{z+}$ or $X^{z-}$ forming

the given binary compound $MX_r$. Such electrodes can consist, for example, of the combinations $M|M^{z+}$ with a cation-conducting electrolyte or $X_2$, $Pt|X^{z-}$ with an anion-conducting electrolyte. ($O_2$, $S_2$, etc. can be used as the substance $X_2$ generating the anions.) Furthermore, each cell can be provided with a pair of electronic or ionic measuring probes playing the role of the corresponding electrodes.

If a direct electronic or ionic current is passed through the cell, concentration polarisation, associated with the presence of a DCS gradient, arises in it. The potential difference between like probes serves as a measure of this polarisation; the method consists of the measurement of the potential difference between the probes as a function of time when the direct current is switched on or switched off. The corresponding theoretical relations have been obtained from the solution of Fick's second equation for a specimen $2L$ long and are compiled in the Table. $\Psi(t)$ denotes the function

$$\Psi(t) = \frac{1}{L}\int_0^L \psi(x,t)\,dx = \frac{1}{L}\int_L^{2L} \psi(x,t)\,dx = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-\frac{(2n+1)^2\pi^2\tilde{D}t}{4L^2}\right], \quad (59)$$

which varies in the range from $\Psi(0) = 1$ to $\Psi(\infty) = 0$.

Time variation of the potential difference between the probes $\phi(0) - \phi(L) = \phi(L) - \phi(2L)$ in Yokota's method when the direct current is switched on and off.

| Electrodes | Probes | $\varphi:0)-\varphi(L)=\varphi(L)-\varphi(2L)$ | |
|---|---|---|---|
| | | establishment of polarisation | decrease of polarisation |
| Electronic | ionic | $\frac{IL}{\sigma}[1-t_i\Psi(t)]$ | $\frac{IL}{\sigma}t_i\Psi(t)$ |
| Electronic | electronic | $\frac{IL}{\varkappa+\sigma}\Psi(t)$ | $-\frac{IL}{\varkappa+\sigma}\Psi(t)$ |
| Ionic | electronic | $\frac{IL}{\varkappa+\sigma}\Psi(t)$ | $-\frac{IL}{\varkappa+\sigma}\Psi(t)$ |
| Ionic | ionic | $\frac{IL}{\varkappa}[1-t_e\Psi(t)]$ | $\frac{IL}{\varkappa}t_e\Psi(t)$ |

Different workers have used cells which constituted various simplified versions of Yokota's cell and have made measurements under conditions where the current was either switched on or switched off. Experimental curves are usually analysed by comparing them with the corresponding approximate expressions for the function $\Psi(t)$.

1. For short times $t \ll L^2/\tilde{D}$, one can use the solution for a semi-infinite medium:

$$\Psi(t) \cong 1 - 2\left(\frac{\tilde{D}t}{\pi}\right)^{1/2}/L \quad . \quad (60)$$

When the partial electrical conductivity is unknown, the CCDC can be determined from the slopes of the $\phi - t^{1/2}$ linear plots in accordance with the formulae in the Table.

2. For long times, only the first term of the infinite series (59) is retained:

$$\Psi(t) \cong \frac{8}{\pi^2}\exp\left(-\frac{\pi^2\tilde{D}t}{4L^2}\right) \quad (61)$$

and the CCDC are found from linear plots in terms of the corresponding semilogarithmic coordinates in the same way as in the potentiostatic method.

A pulse method which is a version of the galvanostatic method, has been used.[6,54,55] This method involves the measurement of the potential difference between the probes when short d.c. pulses, whose duration is small compared with $L^2/2\tilde{D}$, are passed through the specimen.

## 4. The Gravimetric Method

In this method, proposed by Bruce Wagner,[34,56,57] the test specimen is maintained in an atmosphere with a fixed pressure of the non-metallic component $p_{X_2}$ until the attainment of equilibrium. At time $t = 0$, the pressure $p_X$ changes abruptly to a new value. Under these conditions, the concentration of electrons at the end-faces of the specimen for $x = 0$ and $x = 2L$ changes from $N_0$ to a new equilibrium value $N_\infty$, which is established throughout the entire specimen after a time. The change in electron concentration, which is unambiguously related to the change in the stoichiometry of the specimen, corresponds to the dissolution or removal of the non-metallic component from the test specimen and hence to a change in its mass.

Evidently the distribution of concentrations in a plate with a thickness $2L$, which is permeable to the non-metallic component on either side at $x = 0$ and $x = 2L$, is identical with the distribution defined by Eqn.(53), which is calculated under conditions where plates with a thickness $L$ are permeable on one side. Integration of Eqn.(53) with respect to the thickness of the plate permits the calculation of the change in the mass of the specimen as a function of time:

$$\frac{M - M_0}{M_\infty - M_0} = 1 - \Psi(t) \quad . \quad (62)$$

The values of $\tilde{D}$ are determined from the slopes of the experimental $M - t^{1/2}$ curves for short times ($t < 0.32L^2/\tilde{D}$) and $\lg|M_\infty - M| - t$ curves for long times ($t > 0.14L^2/\tilde{D}$) in conformity with the asymptotic formulae (67) and (68), the error of the solutions not exceeding 1%.[58] Furthermore, there exists a region $0.14 < \tilde{D}t/L^2 < 0.32$ in which the two solutions overlap. The error, associated with the representation of the specimen as an infinite plate does not exceed 1%, provided that the thickness of the plate is much smaller than its length and width.

For specimens in the form of a $2a \times 2b \times 2c$ rectangular parallel-piped, the approximate solution corresponding to long times ($|M - M_0| \geq 0.5|M_\infty - M_0|$) is described by the formula[56]

$$\frac{M_\infty - M}{M_\infty - M_0} \approx \frac{512}{\pi^6}\exp\left[-\frac{\pi^2\tilde{D}t}{4}\left(\frac{1}{a^2}+\frac{1}{b^2}+\frac{1}{c^2}\right)\right], \quad (63)$$

while for spherical specimens with a radius $R$ the solution is given by the formula[59]

$$\frac{M_\infty - M}{M_\infty - M_0} \cong \frac{6}{\pi^2}\exp\left(-\frac{\pi^2\tilde{D}t}{R^2}\right) \quad . \quad (64)$$

For specimens in the form of an infinite cylinder, the solution is expressed in terms of Bessel functions and in the general case requires numerical analysis.[60]

The solutions quoted above have been obtained on the assumption of the instantaneous attainment of the equivalent concentration of charge carriers on the surface of the specimen. When the reactions on the surface are slow, the solutions include the corresponding rate constants.[34,61,62]

An important disadvantage of the gravimetric method is its relatively low sensitivity and the associated necessity for the use of comparatively large changes in the composition of the

specimens, which leads to the breakdown of the condition that $\tilde{D}$ is independent of the degree of DCS and ultimately to a considerable uncertainty in the measured values of $\tilde{D}$.

### 5. The Conductimetric Method

This method presupposes the same experimental conditions as the gravimetric method, but differs from the latter by a higher sensitivity (for a suitable disposition of the electrodes and measuring probes).[34,56,63,64] In this method the average electrical conductivity of the specimens serves as a measure of the changes in concentration. It is assumed that the mobility of the current carriers and the effective charge of the diffusing defects remains constant. Under these conditions, the electrical conductivity varies linearly with the concentration of the excess component $N$, i.e. $\sigma = AN +$ const.,[58,60] so that the solutions are obtained from Eqns.(62)–(64) by the simple replacement of $M$ by $\sigma$ and the experimental $\sigma$–$t$ relations are analysed in the same way as in the gravimetric method. If ionic defects with different effective charges are involved in the diffusion, the proportionality between the electrical conductivity and the mass of the specimen breaks down and measurements of these quantities lead to different values of $\tilde{D}$.[26]

### 6. Other Methods

Apart from the relaxation methods described above, mention should be made of the method based on the kinetics of solid-phase reactions[4–6,34,65,66] involving the measurement of the rate of growth of the solid phases in processes involving the oxidation of metals, for example, Fe → FeO, or of lower oxides (chalcogenides) to higher oxides (chalcogenides), for example, FeO → $Fe_3O_4$ → $Fe_2O_3$. It is then assumed that the reaction product (scale) forms a compact non-porous layer in good contact with the metal or lower oxide and the oxidation reaction proceeds under diffusional conditions. According to Wagner's theory,[7] in this case the change in the thickness $L$ of the layer of scale is described by parabolic time law $L^2 = 2K_p t$ with the constant $K_p = \int \tilde{D} d\delta \cong \tilde{D} \Delta\delta$, where $\Delta\delta$ is the total change in the degree of non-stoichiometry along the thickness of the scale, which is independent of time. Wagner[66] also proposed equations for the calculation of the effective CCDC for the formation of multiphase reaction products under diffusional conditions.

Together with the direct measurements of the thickness or mass of the layer of scale as a function of time, in the study of oxidation kinetics one uses also electrochemical cells in which one of the reactants is supplied to the reaction zone by passing a current through a suitable solid electrolyte. For example, in the cell[40,41]

$$(-)\,\mathrm{Pt}\,|\,\mathrm{Ag}\,|\,\mathrm{AgI}\,|\,\underset{\mathrm{Pt}(+)}{\underline{\mathrm{Ag_2S}}}\,|\,\mathrm{NiS}\,|\,\mathrm{Ni} \qquad (65)$$

the electrolyte AgI is used to transfer silver ions from $Ag_2S$ to metallic silver; the layer of the NiS scale grows as a result of the diffusion through it of nickel ions and electrons as well as the sulphur liberated in the electrolysis of the auxiliary layer of $Ag_2S$. The cell e.m.f. then serves as a measure of the chemical potential of sulphur in $Ag_2S$ and hence of the Gibbs free energy of the sulphidisation of nickel. Since the current density is a direct measure of the rate of growth to the layer of scale $dL/dt$ in the parabolic increase of the thickness of the layer, the following time relation should be observed:

$$I = \frac{F}{v} \cdot \frac{dL}{dt} = \frac{F}{v} (K_p/t)^{1/2}, \qquad (66)$$

where $F$ is the Faraday and $v$ the equivalent volume of the scale.

The main disadvantage of the method of solid-phase reactions is the fact that the values of $\tilde{D}$ determined from the measured $K_p$ for known $\Delta\delta$ are averaged over the entire range $\Delta\delta$. In principle, the dependence of $\tilde{D}$ on $\delta$ can be found by differentiating the values of $K_p$ obtained for different cell e.m.f.'s with respect to the corresponding values of $\delta$ at the NiS|$Ag_2S$ boundary. However, since this involves considerable experimental difficulties, the method of solid-phase kinetics is used mainly for the rough estimation of the CCDC.

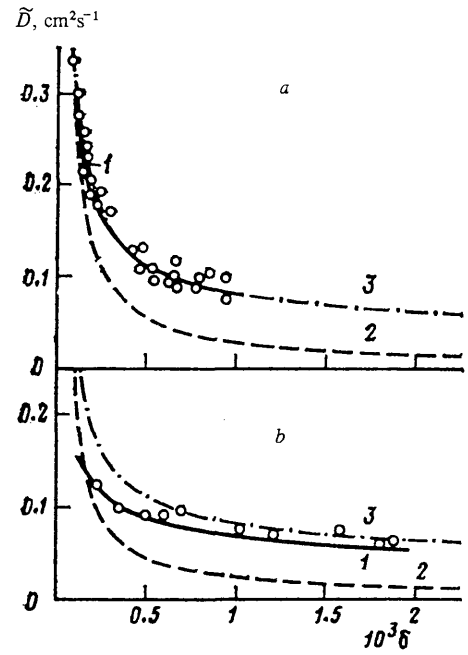



**Figure 4.** Dependence of the CCDC in the $Ag_{2(1+\delta)}S$ (*a*) and $Ag_{2(1+\delta)}Se$ (*b*) cubic phases on the excess content of silver $\delta$ at 200 °C. Circles—experimental values;[53] curves—calculation: 1) according to Eqn.(4); 2) and 3) according to Eqn.(46) for $F_e = 1$ (curve 2) and $F_e$ calculated from the data in Fig.2 (curve 3).

Finally, we may mention the method involving the study of the permeability of solids to gases.[67,68] In this method, the difference between the partial pressures of the non-metallic components $p_{X_2}$ is established on the two sides of a membrane of the test substance and the time variation of the pressure in a calibrated volume as a result of the diffusion of $X_2$ through the membrane is recorded. If the concentration of the gas within the membrane at the inlet is higher than at the outlet and the concentration at the outlet is equal to the initial value, then the pressure at the outlet begins to increase when a time $\tau = L^2/6D$ has elapsed since the establishment of the pressure difference ($L$ is the thickness of the membrane) and subsequently varies linearly with time. The determination of $\tilde{D}$ therefore reduces to the measurement of the intercept $\tau$ made by the experimental linear $p_{X_2}$–$t$ plot.

### 7. Experimental Data

(a) *Silver and copper chalcogenides.* The most reliable CCDC data as a function of the degree of non-stoichiometry have been obtained for silver[36,53] and copper[69,70] sulphides and selenides. The high-temperature cubic phases of these two compounds have a structurally disordered cationic sublattice and exhibit a mixed cationic-electronic conductivity of *n*- and *p*-types respectively. In terms of their electronic properties, they belong to the class of degenerate semi-conductors.

Fig.4 illustrates the results of the direct measurement of $\tilde{D}$ for the $Ag_{2(1+\delta)}S$ and $Ag_{2(1+\delta)}Se$ cubic phases for different excess ($\delta > 0$) contents of silver.[53] The continuous curves *1* were calculated[53] from the phenomenological formula (4) using the experimental random diffusion coefficients of silver and the thermodynamic factor found from measurements of the e.m.f.'s of a galvanic cell. We calculated curves *2* and *3* on the basis of a statistical theory, in accordance with Eqn.(46), which for the compounds considered has the simple form $\tilde{D} = F_e D_{Ag}/\delta$, derived for the first time by Fomenkov.[71] Curve *2* corresponds to the non-degenerate state of the electrons ($F_e = 1$). Curve *3* takes into account the degeneracy; the values of $F_e = F_n$ have been found from the data in Fig.2, using the ratios of the effective mass of the electron to its real mass, $m^*/m_0 = 0.21$ and 0.17, obtained by averaging the literature data[72-76] for the sulphide and selenide respectively.

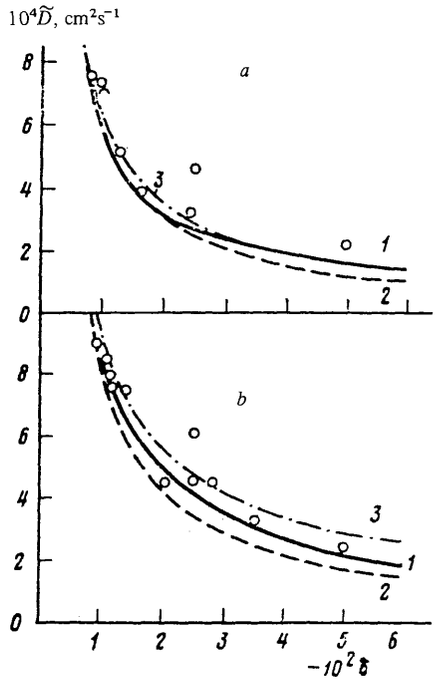



**Figure 5.** Dependence of the CCDC in the $Cu_{2(1+\delta)}S$ (*a*) and $Cu_{2(1+\delta)}Se$ (*b*) phases on the copper deficit at 400 °C. Circles—experimental values;[69,70] curves *1–3* were calculated in the same way as the corresponding curves in Fig.4.

Fig.5 presents analogous data for the $Cu_{2(1+\delta)}S$ and $Cu_{2(1+\delta)}Se$ cubic phases characterised by deficiency of copper in relation to stoichiometry ($\delta < 0$). The circles represent experimental values of $\tilde{D}$.[69,70] In the calculation of curves *1–3* for the stoichiometric sulphide and selenide, the values $D_{Cu} = 6 \times 10^{-6}$ and $8.5 \times 10^{-6}$ $cm^2\ s^{-1}$, which agree within the limits of experimental error with the corresponding $D^*_{Cu}$ for radioactive isotopes,[77,78] were adopted. The effective masses of holes $m^*/m_0 = 7.6$ and 4.6 were taken from Konev et al.[79]

Figs.4 and 5 indicate a satisfactory agreement of the experimental data with the values and relations derived from both the phenomenological and statistical theories, allowance for the degeneracy of the electronic states when $|\delta| > 10^{-3}$ and $10^{-2}$ for silver and copper chalcogenides respectively being important in the latter case. A satisfactory agreement with both theories has also been obtained for the $(Cu_{1-x}Ag_{x+\delta})_2S$ and $(Cu_{1-x}Ag_{x+\delta})_2Se$ cubic solid solutions containing both an excess and a deficiency of the metal and showing maxima on the $\tilde{D}(\delta)$ curves in the vicinity of the stoichiometric composition.[23]

The results of the study of the impedance of the $Pt|\beta\text{-}Ag_{2(1+\delta)}S$ boundary as a function of the excess content of silver in $\beta\text{-}Ag_{2(1+\delta)}S$, which is a non-degenerate *n*-type semiconductor, merit attention.[80]

A readily measurable Warburg impedance, comparable to the resistances of the traditional elements of the equivalent circuit of the cell, was observed. The temperature dependence of the logarithm of the Warburg constant, obtained from the experimental impedance hodographs for a fixed $\delta = 5 \times 10^{-5}$ and the same relation calculated subject to an assumption concerning the CDC of the ions and electrons[1] are almost parallel. The experimental and theoretical values are linked by a constant multiplier of ~0.08, which may be due to the effective area of contact of the solid phases; one can therefore speak of a satisfactory agreement between the theory and experiment in this case also.

(b) *Oxides.* The majority of the experimental data for oxides have been obtained for a large and frequently not measureable difference between the $\delta$ values. The dependences of $\tilde{D}$ on $\delta$ or $p_{O_2}$, which is of greatest theoretical interest, have been investigated for an extremely limited range of compounds.

Reliable data are available for nickel monoxide with a deficiency of the metal, which exhibits Wagner disorder.[81] These data demonstate the constancy of the values of $\tilde{D}$ at 900–1200 °C over a fairly wide range of oxygen partial pressures (from 1 to $10^{-5}$ atm). Analogous results have been obtained for a cobalt single crystal,[56,82] where $\tilde{D}$ is independent of $p_{O_2}$ at 900–1300 °C in the same pressure range.

These results are in good agreement with the expression obtained for $\tilde{D}$ in the case of the vacancy mechanism of the diffusion of cations in the absence of degeneracy of the holes:[34]

$$\tilde{D} = (\zeta_M + 1) D_{VM} . \qquad (67)$$

The validity of Eqn.(67) for $Co_{1-\delta}O$ has also been confirmed by Fryt et al.[35] At the same time Morin's results for $Co_{1-\delta}O$ at 1000 °C [83] demonstrate some (approximately by a factor of 2) increase of the chemical diffusion coefficient $\tilde{D}$ in proportion to $p_{O_2}^{1/4}$ when $p_{O_2}$ $(atm)^{1/4}$ changes from 0.2 to 1. The values of $\zeta_{Co}$, calculated by Eqn.(67), are then close to 2, while the effective charge of the dominant cationic vacancies, determined from the dependence of the electrical conductivity on $p_{O_2}$ is unity at the same oxygen pressures. According to the author,[83] this discrepancy is associated with the anomalies in the mobility of the vacancies, in particular with the dependence of their mobility on $p_{O_2}$ in the region where the $Co_{1-\delta}O$ phase exists.

The available information about the dependence of CCDC on $\delta$ or $p_{O_2}$ for other oxides is not only scarce but frequently contradictory. As an example, one may refer to the results of experiments by different investigators on wüstite $Fe_{1-\delta}O$,[34,45,57] which differ by factors amounting to hundreds for the same temperatures and values of $\delta$ and the dependences of $\tilde{D}$ on $\delta$ obtained by different methods exhibit even qualitative differences. Apparently the main cause of such discrepancy is the complexity of the defect structure of wüstite, in particular its tendency to form extended multiclusters which are not reproducible between different experiments.[2,5] The significant deviations of the defects in wüstite from ideal behaviour are indicated by the observed linearity of the dependence of the logarithm of the activity of oxygen on $\delta$ instead of the expected logarithmic relation.[45]

A considerable variety of the dependences of $\lg \tilde{D}$ on $\lg p_{O_2}$ has been observed for vanadium oxide compounds.[29] The results for the diffusion of oxygen in $VO_2$ and of sodium in $Na_{1/3}V_2O_5$, demonstrating the constancy of the coefficient $\tilde{D}$ within certain ranges of values of $p_{O_2}$, are consistent with the solutions (see Table) for the dominant electronic disorder. On the other hand, for the diffusion of oxygen in $V_2O_5$, $Na_{1/3}V_2O_5$, and $Ca_3Fe_{3.5}V_{1.5}O_{12}$, the horizontal sections on the $\lg \tilde{D}$–$\lg p_{O_2}$ plots are altogether absent and the slopes of their different sections vary from 1/6 to 1, while the theory described can explain only slopes equal to 0 and ±1. The cause of this discrepancy is probably to be sought in the formation of extended defects of the type of shear planes.[2,84] This hypothesis is supported by the observed linear dependence of the partial free energy of oxygen on $\delta$ [85] and also by the low mechanical strength of vanadium oxide compounds and by their tendency to split into separate layers.

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Summarising the above discussion, one may conclude that the joint employment of the phenomenological theory and the statistical-thermodynamic theory based on the model of non-interacting ionic defects can yield much information about the dependence of the CCDC on the degree of CDS or the pressure of the non-metal in the gas phase. The degeneracy of the electrons exerts a significant influence on the CCDC. However, despite the major advances made with the aid of the model of non-interacting defects, its possibilities are apparently close to being exhausted.

The discrepancy between the conclusions derived from the theory and experiment for some of the systems investigated necessitates an increase in the complexity of the existing models, in the first place the allowance for the interaction of ions or point defects and also for the involvement of models of extended defects. It is quite evident that appreciable progress on these lines can be achieved by combined theoretical and experimental studies of both static and kinetic characteristics of solids at the atomic level using microscopic working models of the defect structure and of the mechanisms of the elementary transport steps.

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# Reactions Involving Bimolecular Nucleophilic Substitution at a Vinyl Centre

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The present state of research into reactions involving bimolecular nucleophilic substitution at a vinyl centre is examined. Attention is concentrated on stereochemical questions and also on the influence of various details of the molecular structure of the reacting compound on the kinetics and mechanism of the reactions.
The bibliography includes 167 references.

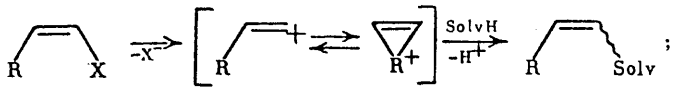
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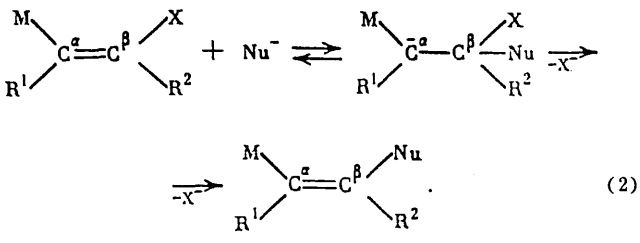
## I. INTRODUCTION

The systematic study of nucleophilic vinyl substitution reactions was initiated by Italian chemists (Modena and others) approximately 25 years ago; this field of organic chemistry is much more recent than the fields which have already become classical, such as those involving the investigation of nucleophilic substitution in saturated compounds, nucleophilic aromatic substitution, or substitution at a carbonyl carbon atom. In order to characterise in broad outline the characteristics of nucleophilic vinyl substitution reactions, it is useful to compare them with the related types of reactions investigated previously, which have been enumerated above, as well as other.

Like the $S_N1$ and $S_N2$ reactions of alkyl halides, nucleophilic vinyl substitution can proceed via unimolecular (1) and bimolecular (2) mechanisms:

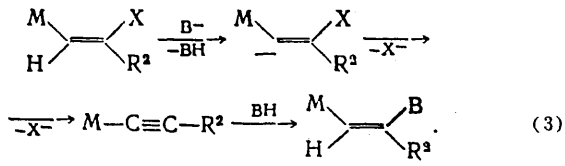


(1)



(2)

Reactions of the first type [reaction (1)] constitute an extensive and fairly completely investigated class of reactions and will not be considered in this review. In Scheme (2) and henceforth Nu represents the nucleophile, $C^{\alpha}$ the carbon atom linked to the activating electron-accepting group M, $C^{\beta}$ the carbon atom linked to the leaving group, and $R^1$ and $R^2$ are the substituents in the α- and β-positions respectively, which can also be the activating or leaving groups. When $R^1 = H$, the substitution can take place under the influence of strong bases via the *ElcB* elimination with subsequent addition in accordance with Scheme (3):



(3)

For brevity, reactions of types (2) and (3) will be henceforth designated as $S_N$Vin reactions.

We shall compare the bimolecular nucleophilic substitution reactions with participation of substrates of different classes. The large class of nucleophilic substitution reactions of the $S_N2$ type at an $sp^3$-carbon atom has been most thoroughly investigated in all respects. However, their comparison with nucleophilic vinyl substitution reactions reveals more differences than common features. In fact, in $S_N2$ reactions the processes in which a bond with a nucleophile is formed and that with the leaving group is ruptured are to a large extent synchronised. The possibility that the bond formation process is appreciably faster than the bond dissociation is ruled out by the impossibility of the expansion of the electron shell of carbon in excess of the octet. On the other hand, in $S_N$Vin reactions of type (2) the formation of a bond with the nucleophile is as a rule rate-determining: this process predominates significantly and frequently wholly over the process in which the bond with the leaving group is broken, which leads to a stable anionic intermediate. As a result, a marked effect of the leaving group on the rate of substitution is observed in $S_N2$ reactions, whereas in $S_N$Vin reactions this effect is absent.

Another fundamental difference follows from the examination of the interaction of the nucleophile with the electrophilic substrate from the standpoint of the theory of frontier orbitals. The highest occupied molecular orbital of the nucleophile (HOMO) interacts with the lowest unoccupied molecular orbital of the substrate (LUMO); in $S_N2$ reactions the substrate LUMO is the σ* orbital of the bond between the carbon atom and the leaving group. The bond formation and dissociation reactions take place along the same axis; this is the reason for the stereochemical result—the Walden inversion. In $S_N$Vin reactions the substrate LUMO is a π* orbital localised in the plane perpendicular to that of the molecule in which the bond with the leaving group is located. The bond formation and dissociation processes are separated

both in time and as regards symmetry and the stereochemical result is determined by the relative contributions and the relative ease of the rotation and inversion processes in the intermediate carbanion—as a rule the configuration is retained.

In terms of the frontier molecular orbitals of the substrate interacting with the HOMO of the nucleophile, the $S_N$Vin reactions resemble the nucleophile substitution reactions of aromatic ($S_N$Ar) and carbonyl ($S_N$Ac) compounds. However, variations in the stereochemical result of the reaction are impossible in either $S_N$Ar or $S_N$Ac reactions and this constitutes one of the powerful instruments for the investigation of the mechanism. Nevertheless, comparison of the reactivities for the reactions of the above classes is frequently useful.

The $S_N$Vin reactions have much in common with nucleophilic addition to electron-deficient olefins (the Michael reaction); the first stage, namely the addition of a nucleophile to the double bond with formation of a carbanion, is the same in these reactions. When necessary, data for $Ad_N$ reactions are therefore resorted to in the present review. $S_N$Vin reactions are frequently complicated by elimination processes with formation of acetylenic or allenic products and sometimes they proceed simply via the $E$–$Ad_N$ mechanism (3). Questions concerning the elimination reaction will therefore be dealt with in so far as it is necessary.

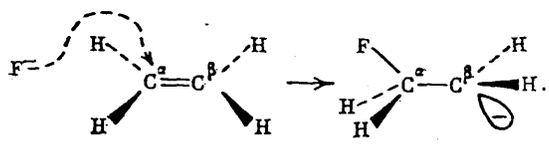
The review does not include purely synthetic studies because this would unjustifiably increase its scope. Attention is concentrated on investigations in the last 10–15 years, since the entire literature on this problem published up to 1968 has been surveyed in Rappoport's review[1] (see also special reviews[2,3]).

## II. QUANTUM-CHEMICAL STUDY

The first calculations on the addition of anions to the C=C bond, modelling the first stage of $S_N$Vin reactions, were carried out by Bazilevskii and Tikhomirov[4] and by Kelsey and Bergman.[5] The addition of $CH_3^-$ to ethylene[4] has been investigated in terms of the "almost π-electron approximation" without the optimisation of the geometry but with allowance for the change in the degree of hybridisation of the reaction centre. Under the conditions of attack in the plane of the π-bond at nearly the tetrahedral angle, $CH_3^-$ undergoes exothermic addition without an activation barrier. Bazilevskii and Tikhomirov[4] concluded that their approximation is inapplicable to calculations on ionic reactions (although calculations on the addition of radicals agree satisfactorily with experiment[6]).

The problem of the elucidation of the relative ease of the nucleophilic substitution at the $sp^3$- and $sp^2$-carbon atoms has been raised.[5] Calculations were made by the extended Hückel method (EHM) with partial optimisation of the geometry for the substitution of hydrogen in ethane and ethylene by the hydride ion. The aim was to compare the heights of the activation barriers, but no barriers were found in either reaction and the authors had to resort to an extremely artificial procedure involving the analysis of a "transition" step. In addition, the attack by $H^-$ on a carbon atom, directed in the plane of the ethylene molecule at right angles to the C=C bond, was considered. Since it is clear from the form of the interacting frontier orbitals that nucleophilic attack takes place preferentially in the plane of the π-bond (in the direction of the π* orbital), this calculation cannot serve as an acceptable model of the $S_N$Vin reaction. Analysis of the mutual orientation of the reactants in the attack by the nucleophile on the π-system[7,8] has indicated that attack by the nucleophile on the π-system[7,8] takes place preferentially in the direction of the bond formed, i.e. at a Nu–C=C angle of approximately 70°. For nucleophiles containing unoccupied 3*d* orbitals, this angle is somewhat greater apparently as a result of 3*d* back bonding: $\pi_{C=C} \rightarrow 3d_{Nu}$.[8]

A non-empirical calculation for the addition of $F^-$ to ethylene[9] has shown that the formation of the *anti*-conformer of the fluoroethyl anion [the orientation of the F atom in relation to the lone electron pair (LEP) of the carbanion was considered] is more favourable than the formation of the *syn*-conformer ($\Delta E$ = 19, 22, and 21 kJ mole$^{-1}$ in terms of the STO-3 GF, 4-31 GF, and 6-31 GF basis sets respectively). This has been explained by the stabilising interaction of the LEP with the σ* orbital of the C–F bond. Calculation of the optimum path leading to the mutual approach of the reactants yielded the following addition scheme:




(4)

When the $C^\alpha$–F distance is changed from 4 to 2.5 Å, the C–C–F angle diminishes to 115.5°, while the further decrease of the distance from 2.5 to 1.4 Å entails a slight increase of the angle to 118.7°, which leads to the *anti*-conformer. There is no activation barrier in reaction (4), which is exothermic in terms of the STO-3 GF basis set: $\Delta E$ = −557 kJ mol$^{-1}$. However, in terms of the 4-31 GF and 6031 GF basis sets, reaction (4) is endothermic with $\Delta E$ = 60 and 67 kJ mol$^{-1}$.[9]

Calculations have been made for reaction (4) by a number of investigators in terms of various approximations. Apart from the study of Bach et al.[9], the instability of the $FCH_2 - CH_2^-$ anion in relation to decomposition has been demonstrated at the 3-21 + GF [10] and 4-31 + GF [11] levels (i.e. with additional Gaussian functions at the C and F atoms). On the other hand, calculation at the 3-21 GF level and in terms of the most refined 6-31 GF* basis set (with polarisation Gaussian functions for the *d* orbitals of heavy atoms) yields a real minimum on the potential energy surface for the β-fluoroethyl anion, the F atom and the lone electron pair being in the *anti*-conformation.[12]

A calculation has been made[13,14] for the interaction of $H^-$, $HS^-$, and $F^-$ with ethylene by the CNDO/BW method with total optimisation of the geometry. Attack by the $H^-$ or $F^-$ ion directed at right angles to the molecular plane of ethylene entails the exothermic formation of the $C_2H_5^-$ or $CH_2FCH_2^-$ anion, while attack at low angles relative to the molecular plane over a distance of approximately 2.5 Å entails the abstraction of a proton with formation of the vinyl anion $C_2H_3^-$ and the $H_2$ or HF molecule. These data agree well with the parallel course of the elimination process in $S_N$Vin reactions which is frequently observed and has been confirmed by experimental data for reactions of anions with fluoroethylenes by the method of ion–cyclotron resonance.[15]

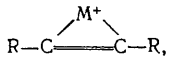
All these calculations refer to the gas phase and lead to barrier-free reactions. The attempt to take into account the influence of the medium even in the simplest version of the solvation model makes it possible to obtain reasonable activation barriers in the CNDO/BW and MINDO/3 methods.[16]

The above calculations were performed for simple ethylenes, while nucleophilic vinyl substitution and addition reactions are characteristic primarily of conjugated molecules with electron-accepting groups. An example of such a calculation is provided by the calculation in terms of the 4-31 GF basis sets of the local minima on the potential energy surface for

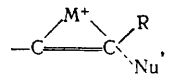
the $CH_2=CH-CHO+Nu^-$ system, where $Nu^- = F^-$ and $CH_3O^-$.[17] In both cases the absolute energy minima correspond to the products of the addition of the anion to the β-carbon atom of the acroleine molecule; the potentially possible competing deprotonation processes are energetically unfavourable. An experimental study of the above reactions in the gas phase by the method of ion–cyclotron resonance confirmed the results of the calculations.[17]

Analysis of the potential energy surface for the $F^- + FHC=CH-CN$ system within the framework of the CNDO/2 and MINDO/3 methods has shown that both reaction pathways, i.e. the addition of the nucleophile and the deprotonation of the substrate, are possible.[18]

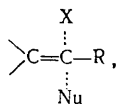
A number of theoretical studies have been devoted to the analysis of the stereochemistry of the nucleophilic vinyl substitution. As a rule, these reactions proceed with retention of configuration of the molecule of the initial substrate (*Z* or *E*). A partial inversion of configuration is sometimes observed[1] and in addition cases of stereoconvergence, i.e. of the formation of the same mixture of isomers of the reaction product regardless of the configuration of the initial substrate, have been described.[19–21] In particular, stereoconvergence is observed for vinyl halides with very strong electron-accepting groups in the α-position or for weakly nucleophilic leaving groups, i.e. in the case of long-lived carbanions. Finally, there exist two types of reactions which proceed, according to the author,[22] with total inversion of configuration when the nucleophile attacks in the molecular plane. These involve the formation of onium cations having the "cyclopropenyl" structure



where M = Ar, S, Br, or I, and the opening of these rings following the attack by an external nucleophile.[22] The transition state in these reactions should have the structure



analogous to the planar structure



which was already considered in an early study by Gold[23] (see also Kelsey and Bergman[5]). In this connection Rappoport[22] concluded that nucleophilic vinyl substitution cannot be regarded as a process proceeding stereospecifically with retention of configuration. The stereochemical specificity should depend on the charge of the leaving group, the capacity for the formation of small rings, and also on the nature of the α- and β-substituents.

Stohrer concluded that configuration is retained in $S_N$Vin reactions and considered a correlation diagram including the orbitals of the reactants involved in the reaction (Fig. 1). In the $R^1R^2\bar{C}^\alpha-C^\beta XYNu$ anion, formed after the attack by the nucleophile, the *p* orbital of the $C^\alpha$ atom tends to achieve maximum stabilisation by overlapping with the antibonding orbitals $\sigma^*_{C^\beta-X}$, $\sigma^*_{C^\beta-Y}$, and $\sigma^*_{C^\beta-Nu}$.[24] As can be seen from Fig. 1, under these conditions the overlap of the $p_{C^\alpha}$ orbital with the $\sigma^*_{C^\beta-Nu}$ orbital is more favourable to the left of the point O and the overlap of the $p_{C^\alpha}$ orbital with the $\sigma^*_{C^\beta-X}$ orbital is more favourable to the right of this point.

The elimination of the leaving group X requires that the axes of the $C^\beta-X$ bond and the $p_{C^\alpha}$ orbital lie in the same plane. According to the diagram in Fig. 1, a kind of enhancement of the effect is observed—the smaller the angle between the $p_{C^\alpha}$ orbital and the $C^\alpha C^\beta X$ plane, the greater the degree of loosening of the $C^\beta-X$ bond owing to the donation of electrons from $p_{C^\alpha}$ to $\sigma^*_{C^\beta-X}$ and the greater the degree of loosening of the bond the greater the degree of further rotation, which ultimately leads to the substitution product with retention of configuration (Fig. 2).

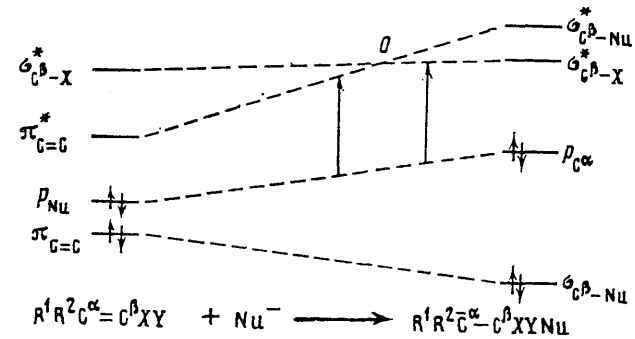



**Figure 1.** Correlation diagram for the stage involving the addition of the nucleophile $Nu^-$ to the olefin $R^1R^2C^\alpha=C^\beta XY$.

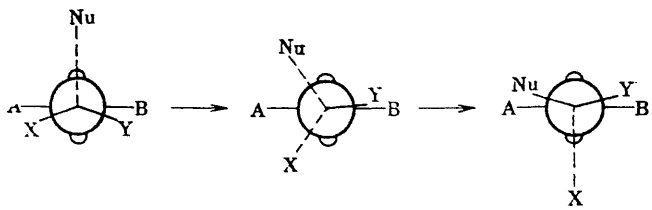
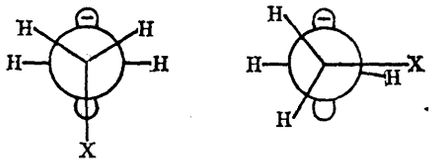



**Figure 2.** Retention of configuration in the synchronous mechanism of the substitution reaction.

An idea with a similar significance has been put forward by Texier et al.[25], who considered the elementary step in the substitution process as attack by the nucleophile at right angles to the molecular plane of ethylene "above" the leaving group within the framework of a synchronous substitution mechanism. This entails the "lateral" binding of the nucleophile to the β-carbon atom.

In the above study[24,25] the retention of configuration in $S_N$Vin reactions was readily accounted for within the framework of a single-stage synchronous substitution mechanism. However, the question of whether nucleophilic vinyl substitution is a single-stage or a multistage process was recently examined in detail by Rappoport,[26] who concluded that so far there have been no reliable examples of $S_N$Vin reactions proceeding via a single-stage synchronous substitution mechanism; on the other hand, the vast majority of the experimental data indicate a two-stage mechanism of

the $S_N$Vin reactions. For a two-stage mechanism, the main question is why the clockwise rotation by 60° in the carbanion formed initially (Fig. 3), which leads to the retention of configuration, is preferable to the anticlockwise rotation by 120°, which leads to the inversion of configuration. On a qualitative level, the preferred rotation of the first type has been demonstrated by Texier et al.[25] As regards calculations of the rotation barriers, there have been two studies devoted to non-empirical calculations for substituted ethyl anions in two conformations (A) and (B):[27,28]



(A) (B)

The calculations were performed in terms of the STO-3GF [27] and 4-31GF [28] basis sets. Overall, the conformation (A) is more favourable than (B) (except in the case where $X = BH_2$) and the energy difference $\Delta E = E^{(A)} - E^{(B)}$ increases with increasing electronegativity of X. This can be explained by the hyperconjugation interaction, which represents the sum of the stabilising interaction of the $p_{C\alpha}$ orbital with $\sigma^*_{C\beta-X}$ and the destabilising $p_{C\alpha}-\sigma_{C\beta-X}$ interaction. The greater the electronegativity of X, the greater the contribution of the stabilising interaction, which is a maximum, as regards the overlap of orbitals, for the conformation (A). It has been noted that the introduction of electron-accepting groups at the carbanionic centre diminishes $\Delta E$; thus, $\Delta E = 23$ kJ mol$^{-1}$ for $CH_2F-C(CN)_2$, while $\Delta E = 42$ kJ mol$^{-1}$ has been obtained for $CH_2F-CH_2$.[27]

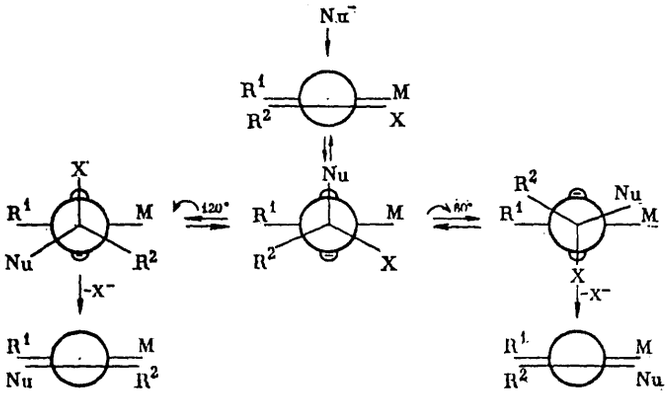


**Figure 3.** A general scheme for stereochemical transformations in the two-step carbanionic mechanism of the substitution reaction.

The application of the idea of the important role of hyperconjugation, put forward by Apeloid and Rappoport,[27] to the general scheme (Fig. 3) leads to the following conclusions: (1) if the energy of the interaction of $p_{C\alpha}$ with $\sigma^*_{C\beta-X}$ is greater than that of the interaction with $\sigma^*_{C\beta-Y}$, then the retention of configuration should be the stereochemical result; (2) when the above quantities are approximately equal, stereoconvergence should be observed; (3) if the energy of the interaction of $p_{C\alpha}$ with $\sigma^*_{C\beta-X}$ is smaller than that of the interaction with $\sigma^*_{C\beta-Y}$, then inversion should take place; (4) the stereochemical outcome is independent of the nature of the nucleophile, because the degree of hyperconjugation of $p_{C\alpha}$ with $\sigma^*_{C\beta-Nu}$ changes by the same amount on rotation by the same angle in either direction; (5) the same ratio of products with retention and inversion of the configuration should be obtained from the *Z*- and *E*-isomers of the substrate. Hence, the retention of the configuration in $S_N$Vin reactions can be explained by the fact that as a rule Y is a hydrogen atom of an alkyl or allyl group and X is a halogen or another group containing a heteroatom and the capacity of the $\sigma^*_{C\beta-X}$ orbital for hyperconjugation is greater than that of the $\sigma^*_{C\beta-Y}$ orbital. There exist examples confirming the validity of this approach.[26,27]

In the above analysis the conclusion that the stereochemistry of the reaction is independent of the nature of the nucleophile appears doubtful especially since experimental data (see Section III) indicate the opposite state of affairs. Indeed, a more detailed analysis[29] has revealed a dependence of the stereochemistry of the $S_N$Vin substitution on the nucleophile and in particular on the energy of the HOMO of the nucleophile. It has been shown that in the case of $S_N$Vin reactions it is essential to take into account the four-electron interaction of the nucleophile HOMO with the substrate HOMO in addition to the two-electron interaction of the nucleophile HOMO with the substrate LUMO usually considered. Evidently the two-electron interaction is stabilising, but the four-electron interaction is destabilising and the latter is more pronounced the lower the energy of the nucleophile HOMO, the destabilising contribution predominating for neutral nucleophiles (for example, $NH_3$). Calculations for the reactions of a large series of vinyl halides with a large set of nucleophiles in terms of the 4-31GF basis set has shown[29] that, with increase of the energy of the nucleophile HOMO, the process becomes more exothermic and there is a shift towards an earlier transition state.† This approach agrees with Hammond's postulate and makes it possible to analyse the joint influence of the nucleophile and the leaving group on the stereochemical result of the $S_N$Vin reaction.

The importance of the mixing of the unoccupied substrate orbitals of the σ* and π* types, which is responsible for the presence or absence of a tetrahedral intermediate in nucleophilic reactions involving the $sp^2$-carbon atom, has been pointed out in the literature,[30] but the authors' analysis is limited to $S_N$Ac and $S_N$Ar reactions.

The most complete theoretical analysis of the stereochemistry and reactivity in $S_N$Vin reactions has been carried out by Cohen et al.[12] Bearing in mind the inconsistency

---

†It is necessary to explain what Bach and Wolber[29] referred to as the "transition state". Having chosen the Nu...C=C distance as the reaction coordinate, they observed the decrease of the height of the energy barrier to rotation about the C–C bond as the nucleophile approaches and the point at which this barrier becomes zero is called the transition state. It is assumed that at this point there is a transition from the process involving the addition of the nucleophile to one involving the expulsion of the leaving group.[29]

between many experimental data with the theory of frontier molecular orbitals and/or the Bell–Evans–Polanyi principle, the authors[12] used the method of correlation diagrams for states in order to set up a general picture describing the stereochemistry and the influence of the nucleophile and of the activating and leaving groups in $S_N$Vin reactions. The heats of reaction, the activation barriers to reactions, and the barriers to inversion in carbanions were calculated, in terms of the double-$\zeta$ basis set using the geometry obtained in terms of the 4-31GF basis set, for eight reactions. The overall correlation diagram for states, including all the reaction stages, is presented in Fig.4. The large difference between the energies of the $\pi$-CT and $\sigma$-CT levels [corresponding to charge transfer from the nucleophile to the $\pi^*$ and $\sigma^*$(C–X) orbitals respectively] predetermines a two-stage mechanism with separation of the stages involving the attack by the nucleophile and the abstraction of the leaving group. The mutual approach of the $\pi$-CT and $\sigma$-CT levels increases the probability of a synchronous process. In essence, this conclusion is analogous to an intuitive idea: the greater the nucleophilicity of the leaving group, the shorter the lifespan of the intermediate carbanion, and hence the closer is the process to being synchronous. The authors[12] were able to describe from a single standpoint the changes in the structure of the transition state, the activation barriers, and certain other reaction parameters in good agreement with experimental data.

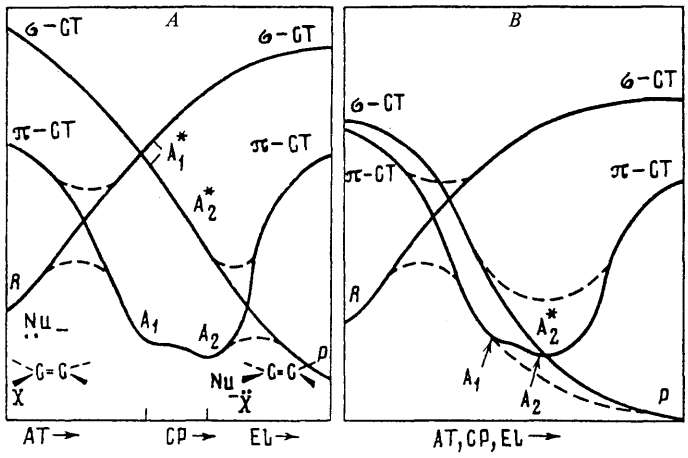
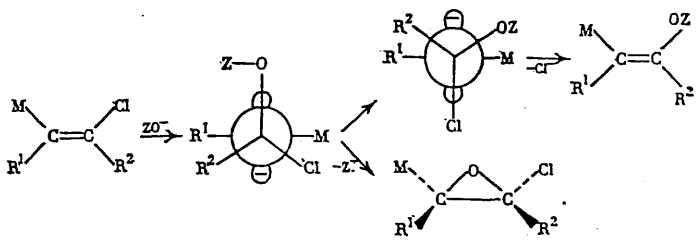



**Figure 4.** Correlation phase diagrams for $S_N$Vin reactions: *A*) two-step mechanism with separation of the steps involving attack by the nucleophile and the abstraction of the leaving group; *B*) one-step synchronous mechanism; AT—step involving attack by the nucleophile; CP—step involving the conversion of the conformer $A_1$ (with a coplanar disposition of the LEP of the carbanionic centre and the bond with the nucleophile) into the conformer $A_2$ (with a coplanar disposition of the LEP of the carbanionic centre and the bond with the leaving group); El—step involving the abstraction of the leaving group; $\pi$-CT—level corresponding to charge transfer from the nucleophile to the $\pi^*_{C=C}$ orbital; $\sigma$-CT—level corresponding to charge transfer from the nucleophile to the $\sigma^*_{C-X}$ orbital; $A_1^*$ and $A_2^*$—excited configurations of the carbanions $A_1$ and $A_2$ respectively.

The competitive course of the $S_N$Vin substitution process and the formation reaction of the epoxide when a chloroalkene is acted upon by the $ZO^-$ nucleophile, where Z is the potential leaving group, has also been discussed:[31]



The subsequent reactions of the carbanion formed in the first stage depend on the relative nucleophilicity of Cl and Z and on treatment with, for example, hypochlorite (Z = Cl), an epoxide is obtained. The rotation barriers have been calculated[31] for a large series of anions of the type $ZQCH_2$–CYY', where Y and/or Y' = H or activating groups ($NO_2$ and CN), while Q = O, $CH_2$, or S and Z = Cl, F, H, OH, $OCH_3$, OCHO, $SiH_3$, or $SH_2^+$ (the calculation was carried out in terms of the STO-3GF, 3-21GF, 4-31GF, and 6-31GF basis sets).

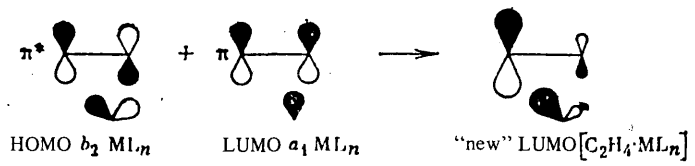



**Figure 5.** The mixing of the orbitals on passing from the symmetrical $\pi$-complex to the $\sigma$-complex.

An increase of the reactivity of the double bond in relation to nucleophiles can be induced not only by the introduction of an electron-accepting group but also by complex formation with transition metals. The causes of such activation are not evident and cannot be accounted for solely by the electrostatic effect, since this phenomenon is observed for both cationic and neutral complex forming agents and for anions and neutral molecules as the nucleophile.[32] At first sight complex formation should in general deactivate ethylene, since the interaction of the LUMO of ethylene with the molecular orbitals of the complex-forming agent $ML_n$ increases the energy of the $\pi^*$ orbital and weakens its interaction with nucleophiles. If the population of the $H^-\ldots C_2H_4$ bond corresponding to the "reasonable" distance of 2 Å is chosen as the reactivity index in the calculation for the interaction of $H^-$ with ethylene activated by complex formation with $ML_n$, then in all cases the population is smaller than in the absence of the complex forming agent. However, when $ML_n$ "slides" along the C=C bond from its centre to one of the carbon atoms (Fig.5), the index increases and for a $\sigma$-complex exceeds that for free ethylene. This results in the mixing of the orbitals and the new LUMO of the complex $[C_2H_4.ML_n]$ is less reactive in relation to the nucleophile than $\pi^*_{CH_2=CH_2}$. The $\pi^*_{C=C}$ orbital naturally predominates in this new LUMO,

but the contribution of $\pi_{C=C}$ is also important, since the $(H^-...\pi^*)$ interaction component of the overall $H^-...C_2H_4$ bond population cannot exceed the analogous value for free ethylene whatever the $ML_n$ shift.

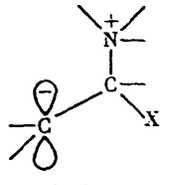
## III. STEREOCHEMISTRY OF THE REACTIONS

The principal electronic interactions determining the stereochemical outcome of nucleophilic vinyl substitution reactions were discussed above. We shall now consider the principal classes of compounds and specific reactions leading to the retention, stereoconvergence, or inversion of the configuration. Since the olefinic carbon atom is achiral, the above terms will be used in relation to the geometrical sequence of the groups compared with the initial compound: the retention of configuration corresponds to the disposition of the nucleophile in the same position relative to the activating group where the leaving group had been located; inversion implies the presence of the nucleophile in the opposite position; stereoconvergence implies the formation of the same mixture of products (or of one product) regardless of the structure of the initial substrate. The term "racemisation" used previously is not entirely exact because the formation of one (most stable) of the two isomers of the product,[1] which is identical with retention of the configuration of one of the isomers and the inversion of that of the other, was frequently regarded as racemisation.

We shall consider initially reactions proceeding in accordance with the direct substitution mechanism (2) via an intermediate carbon atom or zwitter-ion because the stereochemical outcome of reactions involving the elimination–addition mechanism (3) is regulated by the rules governing the addition of nucleophiles to an activated triple bond.[33]

The vast majority of the almost 80 reactions examined in a review[1] take place with retention of configuration. For reactions with amines, the formation of the thermodynamically stable *E*-isomer (with the *trans*-disposition of the activating group and the $R_2N$ residue) is as a rule observed; an exception is ethyleneimine, which reacts with retention of configuration. The causes of the preferential retention of configuration in reactions with anions as nucleophiles were examined above (Section II). There are two alternative explanations (which may also supplement one another) for the formation of the *E*-isomers of enamines in reactions with amines. The first is that a product with retention of configuration is formed initially and then isomerises rapidly to the thermodynamically more stable *E*-enamine. The ease of such postisomerisation is ensured by the strong conjugation of the LEP of the nitrogen atom with the C=C double bond. Thus, it has been shown by NMR that there is free rotation about the C=C double bond in the enamines $(CH_3)_2N-CH = C[C(O)R_2]$ ($R = CH_3$ or $OCH_3$).[34]

The other explanation is based on the zwitter-ionic character of the intermediate complex:



A barrier, due to electrostatic forces, preventing rotation and the attainment of the conformation with a coplanar disposition of the LEP in the carbanionic centre and the bond with the leaving group (the group X is split off in this conformation) arises in the above structure, i.e. the lifespan of the intermediate increases. The possibility of the formation of the thermodynamically most stable conformer of the intermediate, from which the enamine is formed, is thereby achieved.

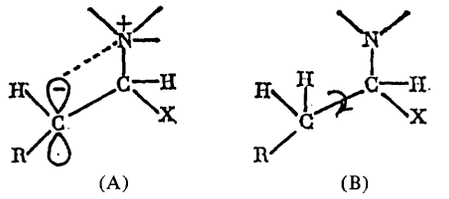
If the first explanation is valid, there should be no differences in the stereochemistry of the substitution reactions with $R_2NH$ or $R_2N^-$ (in the form of sodium amide) as the nucleophile. Unfortunately, reactions with amines and with their anions have not been compared experimentally; the situation is probably complicated by the fact that the amide anions, which are very strong bases, are capable of eliminating the HX group and can thus react via a different mechanism. On the other hand, if the "zwitter-ionic" hypothesis is valid, there should be a fundamental difference between the reactivities of amines and their anions. The retention of the configuration in reactions with ethyleneimine, where effective conjugation of the LEP of the nitrogen atom with the double bond is impossible owing to the pronounced steric strain, supports the view that substitution with retention of configuration takes place also in reactions with other amines and is then followed, as a result of the postisomerisation, by the formation of the thermodynamically more stable *E*-isomer of the substitution product.

The change in the course of the reaction on moving down Group V of the Periodic System, i.e. on passing from amines to phosphines and arsines, has not been studied in detail. It has only been shown that trimethyl phosphite affords the *E*-isomer of the substitution product in reaction with 1,2-di(toluene-*p*-sulphonyl)ethylene.[35] On the other hand, the anion $Ph_2R^-$ reacts with 1,2-dichloroethylene and β-bromostyrenes with retention of configuration;[36–38] the salts of the arsine anion $Ph_2As^-$ also react with retention of configuration.[39] Mention should be made of a study[40] devoted to the stereochemistry of the substitution of the bromine atom in α-bromoacrylic acids or their esters by cuprates, i.e. by the anion $(CH_3)_2Cu^-$; here too retention of configuration was noted in all cases.

Interesting results have been obtained in studies[41,42] of the nucleophilic substitution of bromine in 2-*cis*-β-bromovinyl-5-nitrothiophen. The stereochemistry of the compound was established by $^1H$ NMR from the coupling constant $^3J_{H-H}$. It has been established for a large set of nucleophiles that the substitution proceeds with retention of configuration for tertiary amines, with partial inversion for $ArO^-$, $ArS^-$, and $N_3^-$, and with total inversion for secondary amines and sulphinate anions. Overall, the series obtained is as follows:

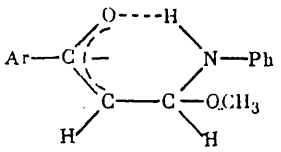
| Nucleophile | $R_3N$ | pyridine | $ArO^-$ | $N_3^-$ | $ArS^-$ | $ArSO_2^-$ | $R_2NH$ |
|---|---|---|---|---|---|---|---|
| Degree of inversion, % | 0 | 0 | 25 | 33 | 50 | 100 | 100 |

The sharp difference in the behaviour of tertiary and secondary amines indicates the important role of the proton, which has also been noted by Rappoport.[1] The strong electrostatic interaction between the positively charged nucleophilic residue and the carbanionic centre in the zwitter-ion probably prevents the clockwise rotation of group (A) by 120° which would lead to inversion. For secondary amines, there is a possibility of the protonation of the neighbouring carbanionic centre (B) and rotation to give the thermodynamically stable conformer is facilitated:



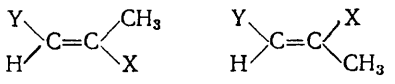
(A) (B) (5)

The importance of the formation of the hydrogen bond in the intermediate zwitter-ion and its influence on the stereochemical result of the reaction are indicated by the results in a study by Chu et al.[43]: the reaction of primary amines ($PhNH_2$) with *E*-3-methoxy-4'-acrylophenones proceeds with inversion of configuration, while the reaction of secondary amines ($PhNHCH_3$) takes place with retention of configuration. The hydrogen-bonded conformation



is the most favourable for the reaction with aniline with the carbanion formed on deprotonation of the zwitter-ion, and the elimination of the methoxy-group from it gives rise to the *Z*-isomer of the substitution product. In the case of *N*-methylaniline there is no hydrogen bond and the sterically less strained *E*-isomer is formed.[43]

A series of studies by French investigators[44-55] has been devoted to nucleophilic vinyl substitution in the esters and nitriles of halogenocrotonic and halogenoacrylic acids. In the reactions of the *Z*- and *E*-isomers of β-halogenocrotonic esters and nitriles (X = Cl or Br; Y = $COOC_2H_5$ or CN), i.e.



with $C_2H_5S^-$ and $PhS^-$ the configuration is retained to an extent greater than 95%.[44] However, in the presence of an excess of the nucleophile Y = CN, the *Z*-isomer of the substitution product is formed either exclusively or preferentially regardless of the configuration of the initial substrate. The author[44] explained this by the isomerisation of the product formed initially in the alkaline medium. The study of the reactions of the same compounds with various amines also revealed a number of characteristic features.[45,46] Only one thermodynamically stable *Z*-isomer of the substitution product is formed in reactions with secondary amines for both Y=CN and Y = $COOC_2H_5$. The nitriles (Y = CN) react with primary amines to form also the *Z*-isomers of the substitution product, while the esters (Y = $COOC_2H_5$) produce almost exclusively (to the extent of 91–98%) the *E*-isomers regardless of the configuration of the substrate. Ethyleneimine reacts with retention of configuration in all cases.

Comparison of these results with the data obtained by the same workers for the reactions involving the addition of various amines to the acetylenic substrates $CH_3-C\equiv C-Y$ (Y = CN or $COOC_2H_5$) [47] permits reliable conclusions about the mechanism of the substitution process. It has been found that both the substitution of the halogen by an amine in crotonic acid derivatives and the addition of amines to the corresponding acetylenic esters and nitriles yield the same product or mixture of products, which led the authors to the conclusion that substitution involves the elimination–addition mechanism (3) via the acetylenic intermediate. The latter is apparently formed under the influence of the strong base $R'O^-$, whose presence in the reaction medium is due to the following equilibrium:

$$RNH_2 + R'OH \rightleftarrows \overset{+}{R}NH_3 + R'O^-.$$

The stereochemistry of the reaction along the initial section of the conversion curve (degree of reaction approximately 5%) has also been investigated.[45] It was found that the product formed under the conditions of kinetic control is thermodynamically stable only in the reaction with ethyleneimine. On the other hand, in the reactions with the remaining amines under the conditions of kinetic control products with retention of configuration were obtained and then isomerised to the thermodynamically stable isomers.[45,46] These results have been confirmed by a special study of the isomerisation of the enamines obtained.[47]

The joint effect of the nature of the leaving and activating groups and of the character of the nucleophile on the mechanism and stereochemistry of the vinyl substitution reactions has been investigated in relation to fluorene- and arene-substituted esters and nitriles of crotonic acid in reactions with $O^-$, $N^-$, and *S*-nucleophiles.[48,49] The fluoro-derivatives react with $C_2H_5O^-$ to form preferentially the *E*-isomer of the product from both the *E*- and *Z*-isomers of the substrate. The iodo-derivatives give rise to elimination products in their reactions with $C_2H_5O^-$—either acetylenes or allenes. Both iodo- and fluoro-derivatives react stereoselectively with "soft" anions ($PhS^-$, $C_2H_5S^-$), forming vinyl substitution products with retention of the configuration. The above compounds react with amines to form mixtures of isomers, the thermodynamically more stable *E*-isomers predominating; *Z*-β-iodocrotononitrile gives rise to an acetylenic derivative. The reaction with ethyleneimine proceeds as a rule with retention of configuration.

The behaviour of the same substrate in reactions with nucleophiles containing a branched hydrocarbon residue, namely $t\text{-}C_4H_9O^-$ and $t\text{-}C_4H_9S^-$, is of interest.[50] Reactions with the highly basic $t\text{-}C_4H_9O^-$ yield exclusively hydrogen halide elimination products, while in the reactions with $t\text{-}C_4H_9S^-$ the composition of the products depends markedly on the nature of the leaving group (the halogen atom) and on the structure of the substrate. On passing from F to Cl and Br and further to I, the content of the elimination and rearrangement products ($CH_2=CX-CH_2Y$) increases, the reaction of the fluoro-derivatives with $t\text{-}C_4H_9S^-$ leads exclusively to substitution products predominately with retention of the configuration, while the Z-isomers of the iodo- and bromo-derivatives afford 90–95% of the acetylenes $CH_3-C\equiv C-Y$ and only 5–10% of the substitution products. The latter (except in the case where X = F) are also formed via the elimination–addition mechanism (3), which has been confirmed by isotope exchange data.

The influence of the α-methyl group was investigated in relation to the *E*- and *Z*-isomers of the compounds $CH_3CX = C(CH_3)COOC_2H_5$ (X = Cl, Br, or I).[51-53] The allene $CH_2 = C = C(CH_3)-COOC_2H_5$ is formed in the reactions with alkoxides as in the case of β-halogeno crotonates, while a large amount of the normal substitution product $CH_3-C(Nu) = C(CH_3)-Y$ is formed in the reactions with *S*-nucleophiles, in contrast to the non-methylated substrate, which gives rise to substitution products with rearrangement, i.e. $CH_2 = C(Na)-CH_2Y$. In this case substitution also proceeds in accordance with the elimination–addition mechanism.[53] The reactions of β-halogenoacrylic esters[54] and β-halogenoacrylonitriles[55] with $C_2H_5O^-$ and $C_2H_5S^-$ also take place preferentially with either the complete retention of the configuration, although isomerisation sometimes occurs in the reaction with the more basic ethoxide anion, or with addition of a second ethanol molecule and the formation of a saturated adduct.

However, the involvement of a larger series of nucleophiles (including the carboxylate, nitrite, and thiocyanate anions) in the reaction with β-chloroacrylonitrile shows that the reaction proceeds non-stereoselectively. The more stable *E*-isomer of the substitution product is formed as a rule in reactions not only with secondary amines but also with the anions quoted above.[56] Reactions with the anions lead to identical or almost identical mixtures of products,

regardless of the configuration of the initial β-chloroacrylonitrile, i.e. stereoconvergence is observed. In addition, one should note that under certain conditions the *Z*- and *E*-β-chloroacrylonitriles are capable of interconversion and this is also true of the products of the substitution of the chlorine in these substances by the RO, RS, and other groups.[57] The substitution reactions under the influence of $RO^-$ and $RS^-$ proceed, as shown also by Biougne et al.[55], with preferential retention of configuration, but under more severe conditions both products and initial reactants isomerise.[57] The energy differences $\Delta G = \Delta G_Z - \Delta G_E$ have been determined for XCH=CHCN, where X = Cl, CN, $CH_3O$, n-$C_4H_9O$, iso-$C_3H_7O$, $C_4H_9S$, t-$C_4H_9S$, and $CH_3COO$. The *Z*-isomer is more stable with the exception of the cases where X = $CH_3O$ and $C_4H_9O$. The differences $\Delta E$ have also been calculated semiempirically by the CNDO/2 method, but the calculated values agree poorly with the experimental data.[57]

The substitution of the fluorine in 2-pentafluoropropenyltetrahydrofuran by alkoxide anions[58] leads to a mixture of the *Z*- and *E*-isomers with the ratio $Z/E = 2.0-5.8$, which differs from that for the initial substrate ($Z/E = 1.9$):

$$R'-CF=CF-CF_3 + RO^- \rightarrow R'-C(OR)=CF-CF_3 + F^-.$$

The author interprets these data from the standpoint of the relative stabilities of the conformers of the carbanion leading to the *Z*- and *E*-isomers of the product, but notes that the *Z*-isomer of the substrate is more reactive and the results obtained for low conversions do not therefore prove the relative stabilities of the conformers.

In the study of the substitution of fluorine in β-fluorovinyl sulphones it has been shown[59] that, on interaction with $CH_3O^-$ and $PhS^-$ in methanol, *E*-$PhSO_2CH=CHF$ gives rise to substitution products with retention of configuration, while the *Z*-isomer produces mixtures with the compositions $Z:E = 1:1.5$ and $3:1$ for the reactions with $CH_3O^-$ and $PhS^-$ respectively. Since the adduct $PhSO_2CH_2CHFSPh$ and the acetylenic sulphone $PhSO_2C\equiv CH$ are stable under the reaction conditions, the non-stereospecificity of the reaction of the *Z*-isomer is apparently associated with the longer lifetime of the carbanion, which permits the establishment of the conformational equilibrium before the elimination of the leaving group.

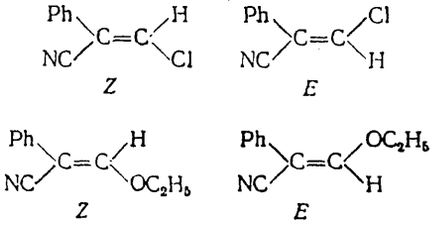
It has been shown[60] that the configuration is retained in the reactions of the *Z*- and *E*-isomers of the nitrile $(CH_3O)_2$.CHCBr=CHCN with piperidine, while the reaction with ammonia leads in all cases to the more stable *Z*-enamine. The data obtained have been compared with the stereochemical result of the reactions involving addition to the corresponding acetylenes.

The majority of the reactions described above have been investigated in proton-donating solvents, although the rule of the preferential retention of the configuration holds also in solvents of the type of dimethylformamide (DMF).[61-64]

Interesting data have been obtained in the study of the reactions of the isomeric β-bromovinyl sulphones $ArSO_2CH=CHBr$ with a series of neutral *N*-, *P*- and *S*-nucleophiles.[65-70] It has been shown that the reactions of these compounds with tertiary amines, containing at least one methyl group, involve substitution with retention of configuration. The reactions of more bulky amines (triethylamine or tri-n-butylamine) lead to the formation of the thermodynamically more stable *E*-isomer of the substitution product. On further branching (in the case of tribenzylamine), the reaction does not take place. The data obtained can be interpreted satisfactorily from the standpoint of steric interactions in the intermediate zwitter-ion.[67] The reactions of β-bromovinyl sulphones with tervalent phosphorus acid amides proceed in a more complex manner.[68,69] Both *N*- and *P*-substitution products are formed, the sulphonyl group also being substituted in a number of instances after the substitution of the bromine atom. The stereochemistry on the whole corresponds to the formation of the less sterically strained *E*-isomers, but it has been established by special investigations (EPR and $^{31}P$ CINP) that these reactions proceed via a one-electron transfer mechanism[70] and cannot therefore be interpreted unambiguously within the framework of the direct vinyl substitution mechanism (2) with participation of an intermediate zwitter-ion. It has been shown in relation to dimethyl sulphide that *S*-nucleophiles react with β-bromovinyl sulphones only under severe conditions, forming methylthiosulphonylmethylenes with retention of configuration and via the following mechanism:[65,66]

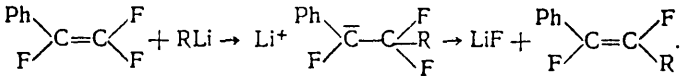
$$ArSO_2CH=CHBr \xrightarrow[100°,50h]{(CH_3)_2S} ArSO_2CH=\overset{+}{C}HS(CH_3)_2\,Br^- \xrightarrow{(CH_3)_2S} \rightarrow ArSO_2CH=CHSCH_3 + (CH_3)_3\overset{+}{S}Br^-.$$

In the presence of more than two substituents at the double bond (in the case of two protons the configuration can be readily determined from the spin–spin coupling constant $^3J_{H-H}$), the question of the unambiguous assignment of the configurations of the substrates and products when the stereochemistry of $S_NVin$ reactions is considered proves to be of fundamental importance. This is well illustrated in relation to a study[71] where the substitution of chlorine in the *Z*- and *E*-isomers of 3-chloro-2-phenylpropenonitrile under the influence of various nucleophiles ($ArS^-$, $C_2H_5O^-$, $N_3^-$, $PhO^-$, piperidine, and morpholine) was investigated:




The authors[71] concluded that the substitution proceeds with retention of configuration of the nucleophile anions, while in the case of amines only one isomer is formed (regardless of the configuration of the substrate), to which the structure of the *E*-isomer was attributed. However, subsequently these data were disproved by other investigators,[72] who claimed that Rappoport and Topol[71] incorrectly assigned the structures of the products of the substitution of chlorine by the ethoxy-group, because comparison of the $^1H$ NMR spectra of the *Z*- and *E*-isomers with spectra calculated in accordance with an additive scheme leads to the opposite assignment. Subsequently it was concluded[72] that reactions with amines involve the initial formation of products with retention of configuration, one of which then rearranges to the more stable product. In contrast to the conclusions reached by Rappoport and Topol,[71] the structure of the *Z*-isomer was attributed to the latter. In the controversy which followed[73] Rappoport agreed with some of the evidence concerning the structure of the substitution product and at the same time pointed out that many discrepancies are associated with the different experimental conditions used by himself[71] and by Le Guillanton and Cariou[72] (concentration, reactant ratio, temperature, etc.) and also dealt critically with the suitability of individual methods for the determination of the structure of compounds, including the stereochemical result of the substitution reaction as one of the criteria of the structure of the initial compound.

Until recently, little was known about the $S_N$Vin reactions with participation of *C*-nucleophiles, i.e. carbanions.[1] Only in recent years have studies been published in which the nucleophilic reactivities of a large series of carbanions were investigated quantitatively in relation to the substitution of fluorine in αββ-trifluorostyrene.[74-76] The reaction takes place stereoselectively with substitution of one fluorine atom:

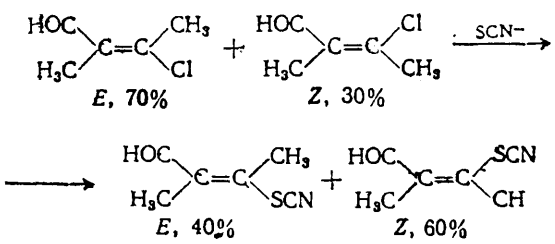


The *trans*-disposition of the fluorine atoms in the substitution product follows unambiguously from the values of $^3J_{F-F}$ in the $^{19}$F NMR spectra (approximately 130 Hz). The substitution of bromine in the *cis*- and *trans*-isomers of β-bromostyrene in its reactions with n-$C_4H_9$Li and n-$C_4H_9$MgBr also proceeds stereospecifically with retention of the configuration.[77]

The reactions of β-halogenovinyl ketones with the soft nucleophile ($PhS^-$) take place with retention of configuration in the initial stage, but the *E*-isomer of the reaction product isomerises at the end of the process to the *Z*-isomer.[78] The causes of this isomerisation are not altogether clear, because *E*-isomers are as a rule more stable. Thus *Z*- and *E*-β-fluoro-*p*-nitrostyrenes react with the same nucleophile ($PhS^-$) to form the *E*-isomer of the substitution product,[79] although in the initial stage under the conditions of kinetic control the *Z*-isomer reacts with retention of the configuration. These compounds react analogously also with $CH_3O^-$, forming *E*-$O_2NC_6H_4SO_2CH=CHOCH_3$.[79] The observed stereochemical differences from the β-chloro- and β-bromo-derivatives have been explained[79] by the longer lifespan of the carbanion in which the leaving group is less nucleophilic ($F^-$).

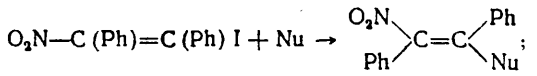
It was noted above (Section II) that, when certain conditions are maintained, stereoconvergence, i.e. the formation of the same mixture of products regardless of the structure of the substrate, can take place but not as a result of post-isomerisation (as happens frequently in reactions with amines or as happened in the study quoted above[78]) but is a consequence of the independent formation of the *Z*- and *E*-isomers from the corresponding conformers of the intermediate carbanion.[80] The number of such examples is small. For "poor" leaving groups (F, OR), this was demonstrated by the studies quoted above,[19,20] while for "satisfactory" leaving groups (Cl, I) stereoconvergence was observed in a series of other investigations.[21,81,82]

The stereoconvergence in substitution reactions with "good" leaving groups is one of the indications of the multistage nature of the $S_N$Vin substitution process[26] and it is therefore useful to examine these cases in greater detail. Korobov et al.[81] (whose study was the first where stereoconvergence was noted for a "good" leaving group despite Rappoport's claims[82]) investigated the following reaction:



A mixture of products of the same composition is also obtained from the individual isomers and it was shown specially that the *Z*- and *E*-isomers are not interconverted under the reaction conditions.[83]

A highly reactive system with a "good" leaving group yields only one product# in reactions with a whole series of nucleophiles:[21]

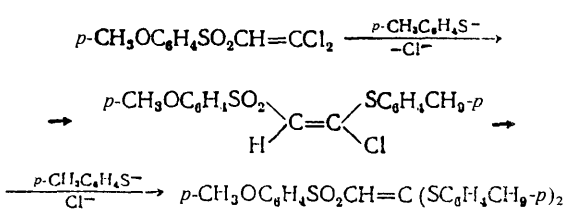


Nu = $SCN^-$, *p*-$C_6H_4S^-$, $N_3^-$, piperidine, or morpholine.

In the somewhat less reactive *Z*- and *E*-$CH_3OCOC(CN)=C(Cl)C_6H_4NO_2$ [82] and *Z*- and *E*-HOC–C(Ph)=C(Ph)Cl [84] systems, the interaction with *p*-$CH_3C_6H_4S^-$, $CH_3O^-$, *p*-$CH_3C_6H_4O^-$, and $Cl^-$ proceeds with either complete or partial stereoconvergence. The aim of the authors of the above studies[82,84] was essentially to find the frontier region between moderately activated substrates, reacting with retention of configuration, and more activated substrates giving rise to complete stereoconvergence.[21] The structure of the isomers put forward in the above communications[82,84] arouses no doubts (in contrast to those in Refs. 71–73), because X-ray diffraction analysis was carried out on individual isomers.

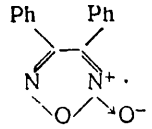
The use of an aprotic dipolar solvent [hexamethylphosphoramide (HMP)] makes it possible to carry out smoothly $S_N$Vin substitution reactions in usually inert unsubstituted chloroalkenes,[62,85] vinyl sulphides, and vinyl selenides.[63,64] It has been shown that, in conformity with the general rule, they react with thiolate and selenolate anions with retention of configuration. It may be that in this case the above result is a consequence of a synchronous substitution process, because this process is most likely to operate precisely in weakly activated or non-activated substrates with "good" leaving groups.[26] The study of the "effect of the element" (see Section IV) can provide an answer to this question, because the magnitude of the "effect of the element" is the most apt criterion for the choice between the synchronous and multistage processes.[20]

Systems with two geminal leaving groups substituted in succession have been investigated and it has been shown that, in the reaction

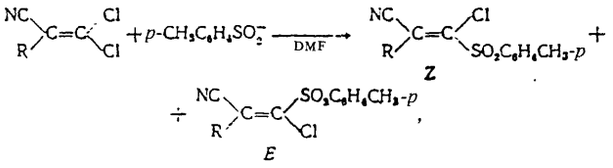


the intermediate 2-chloro-1-*p*-methoxybenzenesulphonyl-2-*p*-tolylthioethylene has the structure of the *E*-isomer.[86] Bearing in mind the general rule governing the retention of configuration in $S_N$Vin reactions, one may conclude that the chlorine atom in the *trans*-position relative to the

#In the case where $Nu = N_3^-$ the product is



α-hydrogen atom is very mobile. This conclusion agrees with the relative reactivities of the *Z*- and *E*-isomers of vinyl halides in $S_NVin$ reactions; overall, the *Z*-isomers are more reactive.[1] In the presence of substituents in the α-position the stereospecificity breaks down:[87]



The *Z* : *E* ratios are 100 : 0, 90 : 10, and 70 : 30 for R = $C_6H_5$, $CH_3$, and t-$C_4H_9$ respectively.[87] The preferential formation of the *Z*-isomer may be associated with the increased energy of the conformer of the carbanion leading to the *E*-isomer owing to the repulsion of the like dipoles (S–O and C–N); the appreciable amount of the *E*-isomer in the case of R = t-$C_4H_9$ is evidently to be explained by the smaller steric strain in the carbanion in the interaction of the $(CH_3)_3C$ and Cl groups than in the interaction of the $(CH_3C)_3C$ and *p*-$CH_3C_4H_4SO_2$ groups.

Despite the fact that the attack by the nucleophile in the plane of the molecule is as a rule less favourable in $S_NVin$ reactions owing to both electronic and steric factors, it can apparently occur in certain special cases (see Section II). Thus the retention of both the configuration of the double bond and the chirality of the substituent in a sterically strained system containing a chiral constituent is believed[88] to be explained best within the framework of the hypothesis that the nucleophile attacks in the molecular plane, since attack in the plane of the π-bond should lead to partial or total loss of chirality.

## IV. QUANTITATIVE DESCRIPTION OF REACTIVITY

### 1. The Influence of the Nature of the Activated Group

Since the occurrence of $S_NVin$ reactions via the mechanism (2) involves the formation of an intermediate carbanion, the increase of the electron-accepting strength of the substituent in the β-position relative to the leaving group evidently accelerates the reaction. In general, this rule is observed but it has not been possible to construct a universal reactivity series for such groups. This is due in the first place to the fact that the quantitative data for the reactivity of systems with different activating groups include data for interaction with various nucleophiles. Thus, assuming that the relative activating capacities of the groups depend only slightly on the nature of the nucleophile, Rappoport[1] proposed the following series:

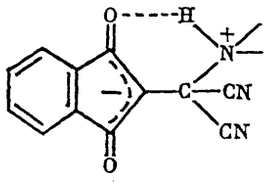
$$2,4\text{-}(NO_2)_2C_6H_3 > PhCO > C_2H_5CO > PhSO_2 > CN > COOC_2H_5 > > PhSO > p\text{-}NO_2C_6H_4 > PhS \gg Cl.$$

However, more detailed analysis using the data of other studies[54,55] yields another series for the reactions of $RO^-$:

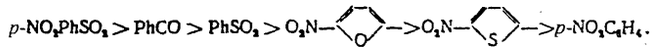
$$CN > SO_2 > CO > SO > 2,4\text{-}(NO_2)_2C_6H_3 > COOR > p\text{-}NO_2C_6H_4.$$

Approximately the same kind of series holds also for the soft nucleophile $PhS^-$, although the reactions can proceed via different mechanisms [mechanism (2) for $PhS^-$ and mechanism (3) for $RO^-$]. The relative reactivity may depend on the structure of the substrate. Thus the *E*-isomer of β-bromo-2,4-dinitrostyrene reacts with $PhS^-$ faster than the *E*-isomer of β-bromovinyl sulphone while the opposite relation holds for the *Z*-isomers.[1]

The reactivity series has been derived in a review[89] from data for the direction of nucleophilic attack on the double bond activated by different groups in CHX = CHY: $NO_2$ > COR > COOR > $PO(OR)_2$. On the grounds of these considerations, the data of Rappoport and Ladkani[90] for addition to $(RCO)_2C = C(CN)_2$ yield the relation RCO > CN, which is confirmed by calculations by the extended Hückel method,[91] but it does not agree with many experimental data. Evidently the nucleophilic attack in αα-diacyl-ββ-dicyanoethylenes on the carbon atom linked to the cyano-groups, although the latter delocalise the negative charge more effectively than the carbonyl groups, can be explained by the fact that the result is not determined solely by the stability of the final carbanion, and in the given instance not even to a major extent, but is determined by the electrophilicity of the carbon atom in the initial state. Furthermore, in the systems investigated by Rappoport and Ladkani[90] the attack of the nucleophile on the carbon atom of the dicyanomethylene group promotes the formation of an intramolecular hydrogen bond and the aromatic character of the anion formed:



Mainly on the basis of the results of their own studies of reactions involving amines,[92–99] Popov et al.[99] proposed the following sequence of groups in terms of their activating strength:



The activating capacity of the nitrogen-group is estimated by comparing the activity data for α-chloro-β-nitrostyrene *E*-$PhCCl = CHNO_2$ and 1,1-dicyano-2-chloro-2-(*p*-dimethylaminophenyl)ethylene $(CH_3)_2NC_6H_4CCl = C(CN)_2$.[100] The authors estimated the ratio $k(PhCCl = CHNO_2)/k[PhCCl = C(CN)_2]$ as 0.22 in terms of the value of ρ for the substituents in the aryl group, which is 1.5, i.e. the electron-accepting properties of one nitro-group are only 4–5 times weaker than those of two cyano-groups. In the case of complete additivity (which naturally does not obtain but such an assumption is acceptable for qualitative conclusion in the given instance[101,102]), the ratio $k(NO_2)/k(CN) = 0.22k(PhCCl = CHCN)/k(PhCCl = CH_2)$ and, since the introduction of the cyano-group in the β-position accelerates the reaction by several orders of magnitude, it is evident that $k(NO_2) > k(CN)$.

Since the first stage of the $S_NVin$ reactions, namely addition to the $sp^2$-carbon atom, is analogous to the first stage in addition to the $Ad_N$ type to electrophiles, a study[103] where the reactivity series has been formulated for $Ad_N$ reactions is of special interest:

$$NO_2 > PhCO > CH_3CO > (C_4H_9)_3P^+ > RSO_2 > (CH_3)_2NSO_2 > > COOCH_3 > CN > \text{4-pyridyl} > PO(OR)_2 > CONHR.$$

In the above series the $COOCH_3$ and CN groups can change places depending on the nucleophile. The following series

follows from the authors' own data:[103]

$$PhCO > PhSO_3 > CHO > CH_3CO > PhCOO > p\text{-}CH_3C_6H_4SO_2 > > CH_3COO > CN > CONH_2 > PO(OR)_2 > p\text{-}O_2NC_6H_4$$

After combining all the available data, it is possible to establish the following expanded reactivity series for electron-accepting groups:

$$NO_2 > PhCO > PhSO_3 > CHO > CH_3CO > (C_4H_9)_3P^+ > PhCOO > > p\text{-}CH_3C_6H_4SO_2 > CN > (CH_3)_2NSO_2 > COOCH_3 > PhSO > > 4\text{-pyridyl} > PO(OCH_2CH_2Cl)_2 > CONH_2 > PO(OC_2H_5)_2 > > CONHR > p\text{-}O_2NC_6H_4 > PhS > Cl.$$

It is of interest that extrapolation of the temperature variations for the few available kinetic data at 200 °C yields a different sequence:

$$PhSO_3 > CH_3CO > PhCO > CHO > PhCOO > p\text{-}CH_3C_6H_4SO_2 > > CN > CH_3COO > CONH_2 > PO(OC_2H_5)_2,$$

i.e. certain members of the series have changed places.

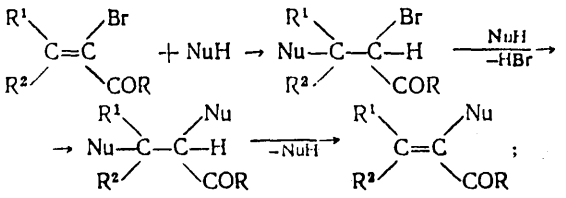
According to Fischer and Jentzch,[104] the dimethyliminomethylene group $(CH_3)_2\overset{+}{N}=CH-$ is a powerful activating group, greatly superior to the carbonyl group, especially in reactions with mild nucleophiles.

The above analysis suggests that the available insufficiently long relative reactivity series for substrates makes it possible to describe satisfactorily the reactivity within the framework of the direct substitution mechanism (2), but their predictive power is fairly weak owing to their dependence on the nature of the nucleophile, the solvent, temperature, etc.

The influence of the second activating group in the β-position with respect to the leaving group is extremely difficult to estimate from the existing investigations, because there are no reactivity data for mono- and di-activated compounds with the same nucleophiles under identical conditions. It is known only that, whereas substrates with a single activating group CN or COOR react solely with aliphatic amines,[49,71] the analogous substrates with two such groups react smoothly with the much less basic anilines.[101] Apparently the electronic influence of two activating groups is to a first approximation additive, provided that the conjugation of each with the double bond does not break down (analogously to the non-uniform variation of the acidities of the substituted methanes with different numbers of CN and $NO_2$ groups[105]). It is noteworthy that the activating capacity of the group X does not always vary in parallel with the $pK_a$ for the corresponding acid $CH_3X$, but a correlation with the rate of ionisation of these acids is sometimes observed.[106]

If the activating group and the nucleophile in the intermediate carbanion are attached to the same carbon atom, then its influence is much weaker, since the effective stabilisation of the carbanion via the conjugation mechanism is impossible, and furthermore, additional steric hindrance arises in the transition state. These two effects can overlap the activating influence of the group. Thus the introduction of the chlorine atom in the α-position in Z-β-chlorovinyl phenyl sulphone accelerates the reaction with $CH_3O^-$ by a factor of 1.3 and with $PhS^-$ by a factor of 1.4,[1] while the introduction of a chlorine atom in the β-position retards the reaction with $CH_3O^-$ by a factor of 1.5 [107] and with $PhS^-$ by a factor of 4.4.[108]

On the other hand, if the activating group is separated from the double bond by the methylene bridge, as in $CH_2=CHal-CH_2CN$, $CH_2=CHal-CH_2COOC_2H_5$,[109] $CH_2=CCl-CH_2SO_2Ph$,[110] or $CH_2=CBr-CH_2PO(OC_2H_5)_2$,[111] then the reaction proceeds via the formation of the allyl anion and then the intermediate allene and not only with hard *O*-nucleophiles but also with soft *S*-nucleophiles.[109] If the electron-accepting group is linked directly to the double bond, as in $R^1R^2C=CBr-COR$,[112] then it polarises the C=C bond in such a way that the Michael addition of the nucleophile takes place initially and then the halogen in the saturated adduct is readily substituted via a mechanism of the $S_N2$ type as in α-halogenoketones. Finally the elimination of the conjugate acid of the nucleophile affords the substitution product:[112]




(6)

The last stage of reaction (6) can yield two different products depending on which of the nucleophile residues is split off. The above example corresponds to regiospecific substitution with retention of the configuration, but there exist examples of the formation of both possible products[113] and of the inversion of regioselectivity.[114]

Finally, the methyl groups in the α- and β-positions in the molecule reduce its reactivity, the effect in the β-position reflecting the electron-donating and steric influence of the $CH_3$ group, while the introduction of the substituent in the α-position rules out in addition the occurrence of reaction via the elimination–addition mechanism (3). In certain cases this can reduce the rate by 4–5 orders of magnitude.[115]

## 2. The Influence of the Nucleophile

It has been noted in a review[1] that the nucleophilicity sequence in $S_NVin$ reactions differs from that for $S_N2$ reactions involving an $sp^2$-carbon atom, but is close to the nucleophilicity series for $S_NAr$ reactions. The corresponding nucleophilicity series are given below:

$PhCH_2S^- > p\text{-}CH_3C_6H_4S^- >$ piperidine $> PhS^- > CH_3O^- > n\text{-}(C_4H_9)_2NH >$ cyclohexylamine $> N_3^- > I^-, Br^-, Cl^-$ (Refs.1, 116) and

$ArS^- > C_2H_5O^-$ > piperidine $> PhO^-$ > morpholine $> N_3^-$ (Ref.71)

for $S_NVin$ reactions,

$$CN^- > HS^- > I^- > SCN^- > \text{aniline} > HO^- > N_3^- > Br^- > PhO^- > Cl^- > F^- \quad \text{(Ref.117)}$$

for $S_N2$ reactions, and

$$PhS^- > CH_3O^- > PhO^- > HO^- > SCN^- > \text{piperidine} > \text{aniline} > I^- > Br^- > Cl^- \quad \text{(Refs.118-120)}$$

for $S_NAr$ reactions.

It is noteworthy that the above series can vary for different substrates (particularly in conformity with Pearson's "symbiosis" effect), and in addition have been obtained for proton-donating solvents. Thus the inversion of the series for $S_NAr$ reactions has been demonstrated in aprotic dipolar solvents:[121,122] $F^- \gg SCN^- > Cl^- > Br^- > I^-$. Even for a single solvent, the relative nucleophilicities can vary fairly widely for slight changes in the substrate structure. Thus piperidine reacts with 1-benzoyl-2-chloro-1-phenylethylene in DMF faster by an order of magnitude than

sodium azide, with 1-benzoyl-2-chloro-1-methylethylene the two nucleophiles react almost identically, while with 1-acetyl-2-chlorocyclopentene the azide ion reacts twelve times faster than piperidine.[123] An analogous behaviour has been observed in ethanol.

Another possibility for a sharp change in the nucleophilicity sequence is associated with the occurrence of the reaction via different mechanisms [mechanisms (2) and (3)]. This is shown particularly clearly for the $PhS^-/CH_3O^-$ pair. $PhS^-$ is usually more reactive than $CH_3O^-$ in reactions via the direct substitution mechanism, for example in reactions with the *Z*- and *E*-isomers of $PhSO_2CH=CHCl$.[1] The reaction with the *Z*-isomer of the bromo-derivative, from which HBr is very readily split off, involves the reversal of this ratio: $k(CH_3O^-) > k(PhS^-)$. For the *E*-isomer of the bromo-derivative, the $E\text{-}Ad_N$ mechanism is less probable and the ratio $k(PhS^-) > k(CH_3O^-)$ is valid. The introduction of the methyl group in the α-position relative to the sulphonyl group rules out the possibility of the elimination of HBr, so that we also have $k(PhS^-) > k(CH_3O^-)$ for $p\text{-}O_2NC_6H_4NO_2.C(CH_3)=CHBr$.[1]

However, despite the lack of a universal scale, the difference between the nucleophilicity series is too great to be attributed to the effects of the medium, non-additivity, etc. The causes of the difference may be more far-reaching and the main cause is apparently the difference in the character and energies of the frontier orbitals. The lowest unoccupied molecular orbital (LUMO) of the substrate in the $S_NVin$ reactions is a π* orbital and its energy is much lower than that of the σ* orbital (the LUMO of the substrate in $S_N2$ reactions). When the highest occupied molecular orbital (HOMO) of the nucleophile interacts with the σ* orbital of the electrophile-substrate, the nucleophilic reactivity is described quantitatively by the Swain–Scott equation.[117] On the other hand, when the LUMO of the electrophile is an orbital of the π* type, for example in carbanions, the Swain–Scott equation does not hold and Ritchie[124] proposed a new $N_+$ nucleophilicity scale in relation to the reactions of nucleophiles with the carbonium ion of the Malachite Green dye. The applicability of this scale to the reactions of nucleophiles with different π-systems, namely carbonyl-containing,[125] aromatic,[126] and electrophilic olefins,[127] was demonstrated subsequently. Consequently the nucleophilic reactivity of the anions in the $S_NVin$ reactions of activated olefins with a low-lying π* orbital should also be described by Ritchie's equation; indeed the rate of reaction of nucleophile anions with substituted 9-methylenefluorenes $R^1R^2C=CXY$ ($R^1$, $R^2$ = fluorenyl; X, Y = H, CN, or $NO_2$) increases in the sequence $CN^- < OH^- < N_3^-$, which is inconsistent with the Swain–Scott scale and is characteristic of Ritchie's scale.[106]

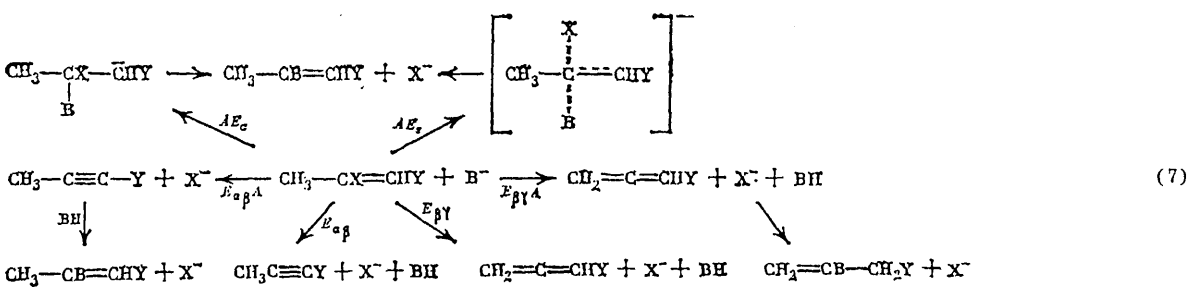
The influence of the nature of the nucleophile on the mechanism of the $S_NVin$ reactions is described satisfactorily in terms of the principle of hard and soft acids and bases. The two electrophilic centres in the substrate molecule, the proton in the α-position and the β-carbon atom§, tend to react respectively with hard and soft nucleophiles. The criteria used to assign the reaction to a particular mechanism are the isotope exchange when the reaction is carried out in deuteriated solvents, the kinetic isotope effect, and the sign of the activation entropy for the reaction. The occurrence of isotope exchange is an essential but not a sufficient criterion of the occurrence of the reaction via the $E\text{-}Ad_N$ mechanism; on the other hand, the positive value of $\Delta S^{\neq}$ indicates reliably the operation of the $E\text{-}Ad_N$ mechanism. The mechanisms (2) and (3) sometimes operate in parallel and the sign of $\Delta S^{\neq}$ then indicates the predominance of one or other mechanism. Only a few examples of the occurrence of the $S_NVin$ reaction with $\Delta S^{\neq} > 0$ have been noted in Rappoport's review;[1] they all take place with participation of $CH_3O^-$ or $C_2H_5O^-$ and only for the *Z*-isomers, i.e. for the *trans*-orientation of the α-hydrogen atom and of the leaving group in the β-position.

In the presence of the methyl group in the β-position, there is a possibility of βγ-elimination with formation of an allene:[44]

$$CH_3\text{—}CX{=}CH\text{—}Y\text{—}\begin{cases}\xrightarrow{RO^-,\,(Y=COOR)} CH_2{=}C{=}CH\text{—}Y \xrightarrow{ROH} CH_3\text{—}C(OR){=}CH\text{—}COOR;\\ \xrightarrow[RS^-,\,(X=Br,\,Y=CN)]{} CH_3\text{—}C{\equiv}C\text{—}CN.\end{cases}$$

As can be seen from the above scheme the elimination can also take place under the influence of the soft nucleophiles $RS^-$.[44] β-Halogenoacrylate esters $C_2H_5OCO\text{—}CH=CHX$ react with $RO^-$ to form a substitution product and the acetylenic ester $C_2H_5OCO\text{—}C\equiv CH$, the content of the acetylene increasing in the sequence X = Cl, Br, and I.[54] The corresponding β-halogenoacrylonitriles also react with $RO^-$ via the $E\text{-}Ad_N$ mechanism, which is indicated by the positive values of $\Delta S^{\neq}$ for the *Z*-isomers, the low negative values of $\Delta S^{\neq}$ for the *E*-isomers, and the high (up to $10^3$) values of the ratio $k_Z/k_E$.[55]

The study of the interaction of β-halogenocrotonates and β-halogenocrotononitriles with various *O*-, *N*-, and *S*-nucleophiles enabled Chalchat and co-workers[49,50,53] to formulate the following general reaction scheme:[50]




(7)

§ The involvement of a halogen atom in the α-position at the electrophilic centre is considered below (Section IV).

The $E_{\alpha\beta}$, $E_{\beta\gamma}$, $E_{\alpha\beta}A$, and $E_{\beta\gamma}A$ mechanisms in Scheme (7) are readily distinguishable even in terms of the structure of the products involved. As regards the mechanisms $AE_C$ (via an intermediate carbanion) and $AE_S$ [synchronous mechanism via the transition state illustrated in Scheme (7)], the authors[50] draw a distinction between them using the analysis of the stereochemistry of the substitution process. If the reaction is stereospecific with retention of configuration, a synchronous process is implied, for which the retention of configuration is the only natural result (see Sections II and III above) but, when a mixture of isomers is produced, the reaction is believed to proceed via a stable intermediate carbanion, whereupon the stereochemical outcome is determined by the relative contributions of the processes involving inversion at the carbanionic centre, rotation in the anion, and the elimination of the leaving group.

On this basis, it was concluded that β-fluorocrotononitriles and β-fluorocrotonates react with almost all *O*-, *N*-, and *S*-nucleophiles via the $AE_C$ mechanism, elimination of the $E_{\alpha\beta}$ or $E_{\beta\gamma}$ type occurring only for the highly basic and bulky t-$C_4H_9O^-$. Bromides behave analogously, although in this case the reaction does not stop at the elimination stage and proceeds via the $E_{\alpha\beta}A$ mechanism for the *Z*-isomers and via the $E_{\beta\gamma}A$ mechanism for the *E*-isomers.[50] Iodides usually react via the $E_{\alpha\beta}$ or $E_{\beta\gamma}$ mechanism ($E_{\beta\gamma}$ elimination with formation of allenes is characteristic of the *E*-isomers), but reactions with soft nucleophiles ($PhS^-$, ethyleneimine) involve substitution via the $AE_S$ mechanism. For α-methylated substrates $CH_3CX=C(CH_3)Y$, $E_{\alpha\beta}$ elimination is impossible and there is a smooth shift from the $E_{\beta\gamma}$ mechanism to the *AE* mechanism on passing from hard ($RO^-$) to soft ($RS^-$) nucleophiles.[53] It is noteworthy that the probability of the occurrence of a synchronous process has been shown[26] to be low and so far there have been no reliable examples. The $AE_S$ and $AE_C$ mechanisms presented in Scheme 7 should therefore be treated as carbanionic mechanisms with short and long lifetimes of the carbanion respectively.

### 3. The Influence of the Leaving Group (the "Element Effect")

The influence of the leaving group is one of the most interesting and informative effects in the study of the mechanisms of $S_NVin$ reactions. Most of the processes associated with this effect were examined in detail previously[1] and in the present Section we shall therefore describe briefly the main principles and will present later data which were not included in Rappoport's review.[1]

The influence of the leaving group is frequently called the "element effect", because the majority of the studies have been carried out for halogen-substituted substrates, usually for the Cl/Br pair. The causes of the fundamental importance of the "element effect" consists in the fact that the vinyl substitution process (2) is a two-stage reaction and the influence of the nature of the leaving group on these stages is markedly different. In fact, if the rate of reaction is determined by the first stage, i.e. by the addition of the nucleophile to the β-carbon atom with formation of a carbanion, then it will increase with increasing electronegativity of the halogen atom: $k(I) \leq k(Br) \leq k(Cl) \leq k(F)$. On the other hand, if the abstraction of the leaving group from the carbanion (the second stage) is rate-determining, then the opposite relation should obtain in conformity with the bond strength: $k(F) < k(Cl) < k(Br) < k(I)$. The latter sequence should hold also for a synchronous process with the simultaneous dissociation and formation of bond, as in $S_N2$ reactions at an $sp^3$-hybridised carbon atom.

Many data for the Cl/Br pair were examined in Rappoport's review[1] and only two instances were quoted for F/Cl. The results of later investigations make it possible to analyse the entire series of halogens from F to I. Thus it has been shown for the compounds $CH_3-CX=CH-Y$ (Y = COOR or CN; X = F, Cl, Br, or I) that the rate of reaction with $C_2H_5S^-$ varies in the following manner: $k(Cl) < k(F)$, $k(Br) \cong k(I)$ (Y = CN) and $k(Cl) < k(F)$, $k(Br) \leq k(I)$ (Y = COOR). The data for the *E*-isomers were used, because in this case the distortions introduced by the contribution of the elimination process are minimal.[49] For the reactions of the same compounds with t-$C_4H_9S^-$, the sequence is somewhat different: $k(F) < k(Cl) < k(Br) < k(I)$, which reflects the contribution of the elimination process.[50] Unfortunately the kinetic data for the reaction with $PhS^-$, which is uncomplicated by the contribution of the $E$-$Ad_N$ mechanism according to the results of Chalchat,[49] are lacking.

Comparison of the data for the interaction of $CH_3O^-$ and $PhS^-$ with β-fluoro-*p*-nitrostyrene with the corresponding data for the β-chloro- and β-bromo derivatives showed[79] that the ratio $k(F)/k(Cl, Br)$ depends on the nature of the nucleophile and amounts to only about 3 for the soft anion $CH_2S^-$. An analogy has been drawn[79] with $S_NAr$ reactions,[128] where this phenomenon has been attributed to Pearson's "symbiosis effect", i.e. to the tendency by substrates containing heavy polarisable leaving groups to bind in the transition state to more polarisable nucleophiles. This has been confirmed by data[129] indicating a decrease of the ratio $k(F)/k(Cl)$ in the series $RO^-$, $R_3N$, $RS^-$, i.e. with increase of the "softness" of the nucleophile, for the reactions of $Ar_2C=CHX$ (X = F or Cl) in DMF. Hence it was concluded that London dispersion forces play a significant role in determing the "effect of the element".

Another aspect of the "element effect" is examined in relation to the reaction of 1,1-dicyano-2-halogeno-2-(*p*-dimethylaminophenyl)ethylenes with anilines in acetonitrile[130] and alcohols.[131] Very low ratios $k(F)/k(Cl)$ (from 0.71 to 3.05) were observed in all the media in contrast to the normally high (approximately $10^2$) values of this parameter. This has been explained by the fact that $k_{exp} = (k_1/k_{-1})k_2$, where $k_1$ is the rate constant for the formation of the zwitter-ion, $k_{-1}$ the rate constant for its decomposition into the initial compounds, and $k_2$ the rate constant for the abstraction of the leaving group from the zwitter-ion. The "element effect" is high ($\gg 1$) for $k_1$, amounts to approximately 1 for $k_{-1}$, and is very small ($\ll 1$) only for $k_2$, because $k_2$ refers to the C–Hal bond dissociation stage (probably, by analogy with reactions of the $S_N1$ type, the "element effect" for $k_2$ amounts to $10^{-2}$–$10^{-6}$).

If the substitution proceeds via the carbanionic mechanism (2), then the "element effect" should not differ sharply for the *Z*- and *E*-isomers of the substrate. On the other hand, for reactions via the $E$-$Ad_N$ (3) mechanism, the dependence on the nature of the leaving group is qualitatively different, because the *Z*-isomers split off HHal much more readily than the *E*-isomers. Indeed, for the esters $C_2H_5OCO-CH=CHX$ (X = Cl, Br, or I), the variation of the rate of reaction with $C_2H_5O^-$ in ethanol for the *Z*-isomers is in the sequence $k(Cl) \ll k(Br) \ll k(I)$, whereas for the *E*-isomers we have $k(I) < k(Cl) \lesssim k(Br)$.[54] For the reactions of the same esters with $C_2H_5S^-$, the "element effect" is much weaker and is in the range 1–2.[54] When the methyl group is introduced in the α-position, the $E$-$Ad_N$ mechanism is ruled out and the "element effect" is close to unity [$k(Br)/k(Cl) = 1.3$].[53] β-Halogenoacrylonitriles $CN-CH=CHX$ (X = Cl or

Br) behave analogously: $k(Br)/k(Cl) = 10^3$ for the *Z*-isomers and 0.82 for the *E*-isomers.[55]

Since strong bases react with activated vinyl halides as a rule via the $E\text{-}Ad_N$ mechanism while "soft" bases react via the direct substitution mechanism (2), large values of $k(Br)/k(Cl)$ are to be expected for the reactions with $RO^-$ and values close to unity for the reactions with $RS^-$. The experimental ratio $k(Br)/k(Cl)$ for ββ-dihalogenovinyl sulphones $ArSO_2CH = CX_2$ (X = Cl or Br) amounts to $10^2$–$10^3$ for the reaction with $CH_3O^-$ and to 1.7–3.3 for the reaction with $ArS^-$.[132]

Values of the "element effect" $k(Br)/k(Cl)$ close to unity (from 0.6 to 1.2), i.e. indicating that the C–Hal bond is not involved in the rate-limiting step, have been obtained for the reaction of $Ar_2C=CHX$ with $ArS^-$ in DMF,[61] but, in the reaction involving the exchange of the halogen X for $^{36}Cl$ under the influence of $Li^{36}Cl$ in DMF, the quantity $k(Br)/k(Cl)$ is much higher (5.1–7.6) and the chloride anion is much less reactive than $ArS^-$ (by 9–10 orders of magnitude).[133]

For 2-halogenovinyl ketones $ArCOCH=CHX$ (X = Cl or Br), the "element effect" has been studied for reactions with both anions[78] and with a wide range of amines.[134] In the case of $PhS^-$, the ratio $k(Br)/k(Cl)$ for the *Z*- and *E*-isomers is in the range 1.7–2.0, while in the reaction of the *Z*-isomer with $CH_3O^-$ a greater "element effect" is observed (approximately 47); for the *E*-isomer, the effect is less than unity (0.64). The high value for the *Z*-isomer is associated with the contribution by the $E\text{-}Ad_N$ mechanism, which has been confirmed by the positive activation entropy ($\Delta S^{\neq} > 0$) [78] and the ratio $k(Br)/k(Cl) < 1$ for the *E*-isomer is evidently caused by the "symbiosis effect" mentioned above. In the reaction of *E*-$PhCOCH=CHX$ with amines,[134] the "element effect" is hardly manifested [$k(Br)/k(Cl) = 0.88$–$1.23$].

The decrease of the ratio $k(Br)/k(Cl)$ with increase of solvent polarity has been demonstrated for the reaction of $p\text{-}O_2NC_6H_4SO_2CH=CHBr$ with piperidine[97] (by comparison with data for the chloro-derivative[135,136]). Hence, it was concluded that in less polar solvents, where the "element effect" is a maximum, the transition state is more "product-like", i.e. it includes a more extended C–Hal bond.

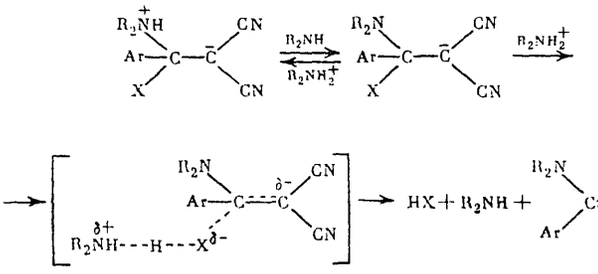
The influence of the leaving group on the substitution of species exhibiting nucleofugacity other than halogen atoms has been investigated.[101,137–139] The ratios $k(Br)/k(Cl)$ [reaction (8)], $k(OSO_2CH_3)/k(Cl)$ [reaction (9)], and $k(OSO_2C_6H_4Br\text{-}p)/k(OSO_2C_6H_4CH_3\text{-}p$ [reaction (10)] were measured:[101]

$$(CH_3OCO)_2C=CHX + ArNH_2 \rightarrow (CH_3OCO)_2C=CHNHAr + HX; \quad (8)$$
X=Cl, Br;

$$(NC)_2C=CHX + p\text{-}NCC_6H_4NH_2 \rightarrow (NC)_2C=CHNHC_6H_4CN\text{-}p + HX; \quad (9)$$
X=Cl, $OSO_2CH_3$;

$$(C_2H_5OCO)_2C=CXC_6H_4NO\text{-}p + HN\langle\rangle Z \rightarrow (C_2H_5OCO)_2C=C\langle N\langle\rangle Z \text{ (with } C_6H_4NO_2\text{-}p\text{)}; \quad (10)$$
X=$OSO_2C_6H_4CH_3\text{-}p$, $OSO_2C_6H_4Br\text{-}p$; Z=O, $CH_2$.

The observed ratios [$k(Br)/k(Cl) \cong 1$, $k(OSO_2CH_2)/k(Cl) = 1$, and $k(OSO_2C_6H_4Br\text{-}p)/k(OSO_2C_6H_4CH_3\text{-}p) = 1.63$–$1.90$] show that the rate-limiting step in the process is the formation of a bond with the nucleophile without the participation of the leaving group and the ratio $k(OSO_2C_6H_4Br\text{-}p)/k(OSO_2C_6H_4.CH_3\text{-}p) > 1$ is caused by the greater electronegativity of the β-carbon atom owing to the more electron-accepting character of the Br atom compared with the $CH_3$ group. By varying the strength of the activating group and by introducing a bulky substituent in the β-position, it is possible to alter the ratio of the rates of the individual elementary stages, so that $k_{exp}$ will include the rate of dissociation of the bond with the leaving group. Indeed, the following ratios hold for the reaction of $(C_2H_5OCO)_2C=CXC_6H_4NO_2\text{-}p$ with various nucleophiles in different solvents: $k(OSO_2CH_3)/k(Cl) = 10$–$60$, $k(OSO_2C_6H_4CH_3\text{-}p)/k(Cl) = 10$–$30$, and $k(OSO_2C_6H_4Br\text{-}p)/k(OSO_2C_6H_4CH_3\text{-}p) = 1.56$ to 2.85, while $k(Br)/k(Cl) = 0.67$–$1.32$ has been obtained for the reaction of $ArANH_2$ with $(NC)_2C=CXC_6H_4NO_2\text{-}p$ and $E\text{-}CH_3OCOC(CN)=CHX$.[137] The dependence on the nature of the leaving group has been observed in the substitution groups with weak nucleofugacity (F, CN, $C_2H_5O$).[138] The fact that the above groups do indeed show "poor" nucleofugacity has been confirmed by the base catalytic effect—the zwitter-ion formed initially reacts with a second amine molecule, abstracting a proton and forming a carbanion, which reacts in its turn with a third amine molecule:



The following sequence in terms of nucleofugacity has been observed: $C_2H_5O(1) \ll CN(10^4) \ll F(10^7)$,[138] which is close to the sequence based on the variation of the $pK_a$: $C_2H_5OH(16) > HCN(9.3) > HF(3.45)$. In the course of the continuation of these studies, the substitution of the $CF_3CH_2O$ group in 1,1-dicyano-2-(*p*-dimethylaminophenyl)-2-trifluoroethoxyethylene was investigated[139] and it was shown that the rate of substitution of the $CF_3CH_2O$ group is higher by 2–3 orders of magnitude than the rate of substitution of the $C_2H_5O$ group and the ratio $k(CF_3CH_2O)/k(C_2H_5O)$ for the amine-catalysed process is greater by an order of magnitude than for the uncatalysed process. This can be explained by taking into account data[130,131,140] for the dependence of the relative contributions of the catalytic and non-catalytic pathways on the nucleofugacity of the leaving group; evidently, the better the leaving group, the less need for the electrophilic cooperation by the solvent or the conjugate acid of the nucleophile.

One must note that the causes of the catalysis of $S_NVin$ reactions by amines may be various. It was believed for a long time[130,131,137,138] that the zwitter-ion formed in the first stage is rapidly and reversibly deprotonated to a carbanion, which then splits off the leaving group and this last stage is in fact catalysed by the amine. However, it has been shown[141,142] (the same idea has been put forward by Rappoport and Peled[139]) that, under certain conditions, in particular in the presence of strong steric hindrance, the rate-limiting stage may be the deprotonation of the zwitter-ion. Thus, in contrast to the expected diffusion-controlled values of the rate constant ($10^8$–$10^9$ $s^{-1}$), values up to $10^3$ $s^{-1}$ were obtained, i.e. smaller by a factor of approximately $10^6$.[141] In many cases this permits a critical revision of the causes of the catalysis of $S_NVin$ reactions by amines with participation of "poor" leaving groups.[142]

In the only study where the leaving group was varied for a series of substituents (in the sense that it can be described by a single set of σ constants) the substitution of the ArO group in *E*-4-aryloxybut-3-en-2-zones by various *N*- and *S*-nucleophiles was investigated.[143] The reaction proceeds via the direct substitution mechanism and the rate

is determined by the stage involving the addition of the nucleophile to the double bond. The reaction rate increases with enhancement of the electron-accepting strength of the substituent in the benzene ring, as the nucleofugacity of the leaving group increases, but the Hammett constants $\rho$ (the $\sigma$ constants were calculated from data for the ionisation of the corresponding phenols) are very low: 0.11 for the reaction with aminoethanol and 0.14 for the reaction with *N*-acetylcysteine, which also confirms the low degree of dissociation of the ArO...C bond in the transition state.

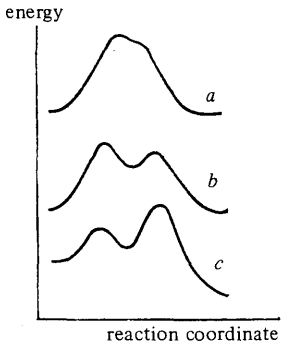



**Figure 6.** The energy profile for nucleophilic vinyl substitution reactions: *a*) one-step mechanism; *b*) two-step mechanism in which attack by the nucleophile is the rate-limiting stage; *c*) two-step mechanism in which the abstraction of the leaving group is the rate-limiting step.

The concept of a variable transition state in $S_N$Vin reactions has been recently put forward and elaborated in detail.[26,144] It is suggested that the position of the transition state and also the presence and structure of the possible intermediates depend greatly on a series of external and internal factors, in the first place on the strength of the activating groups and on the nucleofugacity of the leaving group. We shall examine the overall variation of the "element effect" as a function of the stability of the carbanion. In the limiting case where the carbanion is extremely unstable, it can degenerate into a transition state, and the substitution can proceed as a synchronous process with a high "element effect" $k(Br)/k(Cl) > 1$ (Fig.6, curve *a*). With increase of the stability of the carbanion, so long as $k_{exp} = k_1$ the "element effect" should be approximately 1 (Fig.6, curve *b*). Finally, for very stable carbanions, where $k_{exp} = (k_1/k_{-1})k_2$, the "element effect" should again increase due to $k_2$ (Fig.6, curve c). In order to achieve the last situation, a study has been made[145] of the substitution of a halogen in the most activated system among those investigated kinetically hitherto, namely tricyanovinyl halides. However, the value of the "element effect" $k(Br)/k(Cl)$ found amounted to only 2.4, i.e. did not exceed the usual values. The authors explain the result[145] by the earlier transition state in the reaction involving the abstraction of the leaving group from the carbanion (see, for example, Thomas and Stirling[146]) and concluded that the "element effect" precludes the identification of the rate-determining state—the formation of the carbanion or the abstraction of the leaving group from the latter.

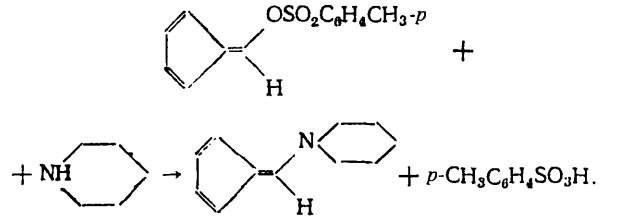
## 4. The Influence of the Solvent

The influence of the solvent on the rates and mechanism of $S_N$Vin reactions has been investigated mainly for reactions with amines. A single study,[123] permitting a comparison of the rates of the reactions of certain β-halogenovinyl ketones with piperidine and the azide ion in ethanol and DMF, is quoted in Rappoport's review.[1] Only a slight acceleration (and sometimes even a retardation) of the reaction with piperidine in DMF compared with ethanol has been observed, the acceleration of the reaction with $N_3^-$ being much greater (by a factor of 4–40). However, a dipolar aprotic solvent does not always accelerate the reaction—the rate of reaction of carbanions with αββ-trifluorostyrene in aprotic dipolar solvents increases as ethanol is added.[147] In this case the solvent influences mainly the solvation of the transition state in which a partial negative charge is transferred largely to fluorine atoms.

The influence of the solvent on $S_N$Vin reactions involving amines has been studied systematically in a series of investigations.[92,95,97,135,136,148–150] Thus the change from polar solvents (*o*-dichlorobenzene, nitrobenzene) to non-polar solvents (n-alkanes) diminishes the rate of reaction of β-halogenovinyl ketones;[92] it is of interest that this retardation is much smaller (by a factor of 4–6) for primary and secondary amines than for tertiary amines (by a factor of $10^3$). This indicates an insignificant increase of the polarity of the transition state compared with the initial state for amines containing a proton in the NH group and the sharp increase of its polarity in the absence of such a proton. The polarity of the zwitter-ion is probably reduced for primary and secondary amines owing to the formation of a hydrogen bond and ultimately the protonation of the carbanionic centre (5); hence the reason for the very sharp difference between the sensitivities to changes in solvent polarity. A monotonic increase in the rates of reaction of β-halogenovinyl sulphones[97,135] and β-bromo-*p*-nitrostyrene[148] with piperidine with increase of the dielectric constant ε has been observed for solvents whose interaction with the reactants is of the type of non-specific solvation. In addition the "element effect" diminishes steadily with increase of ε (see Section IV).

In their analysis of the interaction between substrate structure and polarity of the medium, Litvinenko et al.[136] obtained a non-additive equation reflecting the decrease of the sensitivity to solvent polarity with increasing electrophilicity of the substrate.

A varied series of solvents, including non-polar, polar, aprotic, and dipolar aprotic solvents, has been investigated for the reaction of β-halogenovinylnitrofuran with piperidine.[95,149,150] Naturally it was not possible to isolate any one parameter characterising the influence of solvents of such different nature, but, bearing in mind the possibility of the formation of solvation complexes with different structures, the influence of the acidity in the case of alcohols, the polarisability, the formation of hydrogen bonds with the amine, etc., the authors[95] explained successfully all the observed changes. The influence of solvents on the rate of reaction of piperidine with 6-(toluene-*n*-sulphonyloxy)-fulvene has been accounted for analogously:[151]

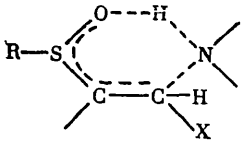


The acceleration of the reaction in the series of alcohols $CH_3OH < C_2H_5OH <$ iso-$C_3H_7OH$ is associated with the decrease of the acidity of the alcohol and hence with the increase of the activity of the amine, while the acceleration of the reaction in acetonitrile compared with chloroform is due to the increase of solvent polarity. Comparison of the data of two investigations by Rappoport and Ta-Shma[130,131] shows that the replacement of acetonitrile as the solvent[130] by alcohols[131] in the reactions of 1,1-dicyano-2-(*p*-dimethylaminophenyl)-2-halogenoethylenes with anilines leads to a change in the reaction order with respect to amines. Whereas in acetonitrile the reaction is of second order with respect to the amines where Hal = F and of "almost" first order for Hal = Cl, in alcohols the reaction order with respect to the amine decreases and is more than unity but less than two for fluorine and is unity for chlorine. Since the amine participates in the stage involving the abstraction of the leaving group, evidently an increase in the acidity of the solvent, which competes with the amine at this stage, reduces the order of the reaction with respect to the amine (an analogous decrease of the order with respect to the amine with increasing "proton-donating capacity" of the medium had been known previously for $S_NAr$ reactions[152]). On passing to "poor" leaving groups in the same substrate, the trend persists—the amine-catalysed process involving the abstraction of the leaving group predominates in acetonitrile and the non-catalysed process becomes the main reaction pathway in alcohols.[138]

As was to be expected, an increase in the polarity of the medium (the change from the composition $CCl_4 : CH_3CN = 1:1$ to $CCl_4 : CH_3CN = 1:3$) accelerates the reaction. The rate of reaction in various alcohols is determined by the relative acidities and is a maximum for the least acid alcohol.[138] The substitution of various leaving groups by amines in $(C_2H_5OCO)_2C=CXC_6H_4NO_2$ has been investigated in acetonitrile, THF, and ethanol. In most cases the rate of substitution increases in the sequence $C_2H_5OH <$ THF < $CH_3CN$. The changes are small and for the THF/$CH_3CN$ pair can be explained by the changes in the polarity of the medium. The low rate of reaction in ethanol is due to the solvation of the ground state as a result of the formation of the hydrogen bond with amine, which is reflected also in the activation parameters of the reaction. $\Delta H^{\neq}$ increases owing to the necessity to dissociate the intermolecular hydrogen bond and $\Delta S^{\neq}$ becomes less negative, since such dissociation entails the "unfreezing" of some of the degrees of freedom.[137] The reactivity changes analogously in the series THF, $CH_3CN$, DMSO.[139] In all three media electrophilic assistance with the abstraction of the leaving group is lacking and the observed effects are associated with the change in the dielectric constant of the medium.

The accelerating effect of an aprotic dipolar solvent in the reactions of nucleophile-anions should be much stronger than for amines. Indeed, the substitution of the halogen atom in β-halogeno-*p*-nitrostyrenes by sodium methoxide in methanol is accelerated by a factor of $10^4$–$10^6$ after the addition of 85% DMSO. The increase of the DMSO content then entails an increase of the contribution of the HX elimination step.[153]

The transition state in the reactions of activated vinyl halides with amines is either an open-chain zwitter-ion or, in the case of hydrogen bond acceptor groups (CO, SO etc.), a cyclic structure of the type



The transition state of the open-chain zwitter-ionic type is more polar than the initial reactant, while the formation of a hydrogen bond can diminish the polarity of the system. Hence one may expect that in polar media, where the open-chain zwitter-ionic structure is more favourable, the rate of reaction will increase with increase of ε, while in media of low polarity it will decrease. This has not been observed for β-halogenovinyl ketones[92] but for β-halogenovinyl sulphoxides the cyclic structure is more favourable in media with low and moderate polarity, because the SO group is a better hydrogen bond acceptor than the CO group.[154] As a consequence, the rate of the reaction

$$E\text{-}p\text{-}O_2NC_6H_4SO{-}CH{=}CHBr + C_5H_{10}NH \rightarrow E\text{-}p\text{-}O_2NC_6H_4SO{-}CH{=}CH{-}NC_5H_{10} + C_5H_{10}\overset{+}{N}H_2Br^-$$

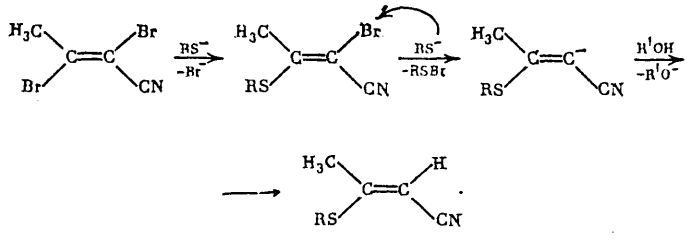
in aprotic solvents falls with increase of ε from 2 to 9 and then increases as ε increases further to 37.5.[154]

## V. REDUCTION AND REARRANGEMENT PROCESSES IN NUCLEOPHILIC VINYL SUBSTITUTION REACTIONS

All the reactions examined above are initiated by the attack of the nucleophile either on the β-carbon atom [mechanism (2)] or on the α-hydrogen atom [mechanism (3)]. However, in the molecules of vinyl halides, which are the most typical substrates in $S_NVin$ reactions, yet another centre potentially susceptible to attack by the nucleophile is present, namely the halogen atom. The ease of halogenophilic substitution increases with increasing electronegativity of the carbon atom linked to the halogen, i.e. in the sequence $C_{sp^3} < C_{sp^2} < C_{sp}$. Thus halogenophilic substitution in halogenoacetylenes is encountered fairly frequently,[155] while in the series of saturated compounds it is necessary that several electron-accepting groups should be present at the C–Hal bond.[156,157] Vinyl halides occupy an intermediate position and in the absence of an electron-accepting group in the α-position halogenophilic substitution usually does not occur. In the presence of two vicinal halogen atoms at the double bond, the halogen atom occupying the α-position which is geminal in relation to the activating group has a greater tendency to undergo halogenophilic attack. In the reaction of 3-halogeno-2-butenonitriles with thiolates the halogen atom is substituted,[44,49,53] while 2,3-dihalogeno-2-butenonitriles give rise to either disubstitution products or products of substitution with reduction depending on the nature of the halogen:[158]

$$CH_3CX{=}CXCN + RS^- \rightarrow \begin{cases} CH_3C(SR){=}C(SR)CN & (X{=}Cl); \\ CH_3C(SR){=}CHCN & (X{=}Br). \end{cases}$$

2,3-Dihalogenocrotonate esters $CH_3CX=CXCOOC_2H_5$ react analogously.[159] The reduction product is formed in the second reaction as a result of the halogenophilic attack on the bromine atom in the α-position:



When the halogen is substituted by the dimethylcuprate anion in β-halogenostyrenes[144] or in β-bromoacrylic acid derivatives,[40] reduction products are also formed, probably as a result of the halogenophilic attack by $(CH_3)_2Cu^-$. The monohalogenovinyl sulphones $PhSO_2CH=CHBr$ and $PhSO_2CH=CHI$ are formed as cyclic products in the reaction involving the substitution of bromine by iodine in the ββ-dibromovinyl sulphone $PhSO_2CH=CBr_2$ on treatment with sodium iodide.[160] The higher content of β-iodovinyl sulphone compared with β-bromovinyl sulphone is consistent with the relative ease of the halogenophilic attack on the iodine and bromine atoms.

Until recently, the available information about the rearrangements in the $S_NVin$ reactions was restricted to double bond migration reactions in the presence of the $CH_3$ group in the β-position:[49,50,53]

$$Y-CR=CX-CH_3 + NuH \xrightarrow[-HX]{} Y-CR=C(Nu)-CH_3 + Y-CHR-C(Nu)=CH_2, \quad (11)$$

or in the presence of the methylene bridge between the activating group and the double bond (the reverse reaction):[52,109]

$$Y-CH_2-CX=CH_2 + NuH \xrightarrow[-HX]{} Y-CH_2-C(Nu)=CH_2 + Y-CH=C(Nu)-CH_3. \quad (12)$$

The mechanism of both rearrangements consists of the formation of the intermediate allene $Y-CR=C=CH_2$, common to reactions (11) and (12), which can subsequently give rise to both αβ- and βγ-adducts. The product $Y-CHR-C(Nu)=CH_2$ is formed under the conditions of kinetic control owing to the greater stability of the anion $Y-\bar{C}R-C(Nu)=CH_2$ compared with $Y-CR=C(Nu)-\bar{C}H_2$, while the product $Y-CR=C(Nu)CH_3$ is formed under the conditions of thermodynamic control (as a consequence of the conjugation of its double bond with the electron-accepting group).

A new type of rearrangement in nucleophilic vinyl substitution reactions has been discovered recently:[161,162]

$$PhSO_2CH=CX_2 \xrightarrow{\text{KF.18-crown-6}} PhSO_2\diagdown\!\!\diagup C=C\diagup\!\!\diagdown H \quad (13)$$

X = Cl, Br.

In reaction (13) the rearrangement is not accompanied by substitution, but in other cases both processes take place:[132,162,163]

$$RSO_2CH=CCl_2 \xrightarrow[-Cl^-]{I^-} RSO_2CI=CHCl \begin{cases} \xrightarrow{\text{KF.18-crown-6}} RSO_2CI=CHF; \\ \xrightarrow{CH_3E^-,\ CH_3OH} RSO_2CI=CHOCH_3. \end{cases} \quad (14)$$

A rearrangement with substitution under the influence of amines takes place in compounds with similar structures:[164]

$$E\text{-}RSO_2CCl=CClSO_2R + R'NH_2 \longrightarrow (RSO_2)_2C=C(NHR')_2 + \overset{+}{R}NH_3Cl^-. \quad (15)$$

We may note that in 1977 in a review on 1,2-anisotropic rearrangements this type of rearrangement involving ethylenes was classified as "unknown but susceptible to observation" and the author expressed surprise that it had not yet been discovered.[165]

The mechanism of the rearrangement has not been fully elucidated; the first stage of reaction (13) is evidently the deprotonation of dihalogenovinyl sulphone, which is confirmed by the occurrence of the rearrangement under the influence of bases other than $F^-$.[162] The 1,2-migration of the halogen may take place in the vinyl anion formed, leading to the *Z*-isomers of the reaction products on subsequent protonation. In reactions (14) and (15) the vinyl anion can be formed as a result of the halogenophilic attack on the chlorine atom, although the authors[164] have not discussed the mechanism of the observed rearrangement. The prohibition of the 1,2-migration in anions by orbital symmetry is in this case probably proved owing to the contribution by a structure of the carbene type $RSO_2-\ddot{C}=\bar{C}X_2$, which creates an electron deficiency at a formally carbanionic centre—the α-carbon atom. We may note that the contribution of structures of the carbene type is a characteristic feature of vinyl anions and vinyl cations, in contrast to their saturated analogues; it had been considered earlier in the case of vinyl cations in order to account for their anomalous behaviour in rearrangements.[166]

The hypothesis of the 1,2-migration of the nucleophilic group in the anion was put forward[167] to explain the anomalous mode of the elimination reaction:

$$PhCH(OCH_3)-CH_2SO_2R \xrightarrow[-H^+]{} PhCH(OCH_3)-\bar{C}HSO_2R \rightleftarrows \rightleftarrows Ph\bar{C}H-CH(OCH_3)-SO_2R \xrightarrow[-RSO_2^-]{} PhCH=CHOCH_3.$$

The alternative mechanism—the elimination of HX and addition with inversion of the configuration—is unlikely in reaction (13), because the formation of 1,2-dihalogenovinyl sulphones by the addition of HX to the acetylenes $RSO_2C\equiv CX$ conflicts with the rules governing the regioselectivity in addition to activated acetylenes.[155]

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Thus the study of the nucleophilic vinyl substitution reactions, which had not been hitherto regarded as an independent class of reactions in any of the modern textbooks of the theoretical principles of organic chemistry (apart from the fundamental monograph by C.K.Ingold, who devoted several pages to them), nowadays constitutes an entirely independent field of study characterised by interesting reactions, specific features, and significant differences from related types of reactions. In assessing the prospects for the development of the research in this field, one may expect that the most interesting results will be obtained in the study of the influence of the leaving group (previously restricted as a rule to halogen atoms), the influence of the solvent (it has been hardly studied for reactions with nucleophile-anions), the competition course halogenophilic processes, and finally, new rearrangements accompanying the nucleophilic vinyl substitution reactions.

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# Polyhedral Metallaboranes, Metallacarbaboranes, and Metallaheteroboranes with the $\eta^5$-$C_5H_5Fe$ Fragment in the Polyhedron

L.I.Zakharkin, V.V.Kobak, and G.G. Zhigarëva

The literature data on the synthesis and properties of polyhedral boranes, carbaboranes, and heteroboranes with the $\eta^5$-$C_5H_5Fe$ fragment in the polyhedron are surveyed and described systematically.
The bibliography includes 74 references.

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## I. INTRODUCTION

One of the most important discoveries in chemistry during the last twenty years has been the synthesis of metallacarbaboranes—a new class of compounds with a polyhedral structure. The rigorous development of this field of chemistry has led to the preparation of an enormous number of compounds differing in their geometry, the number of vertices, and various combinations of boron and carbon atoms, a heteroatom (usually the atom of a Group II–VI non-transition element), and a transition metal atom. At the present time one can speak of the establishment of a new field of chemistry—the chemistry of polyhedral metallacarbaboranes and metallaboranes. The number of new metallacarbaborane structures is large and increases consistently every year, so that the reviews published in the literature in recent times have either become obsolete, or reflect only individual studies by certain groups of investigators,[1-4] or have been devoted to narrow specialist questions in the chemistry of metallacarbaboranes.[5-9] The present review deals with the structure, methods of synthesis, and certain reactions of polyhedral boranes, carbaboranes, and heteroboranes with the CpFe group† in the polyhedron. These compounds are a link between ferrocene, on the one hand, and *commo*-ferracarbaboranes, on the other. The structural and electronic analogies between ferracarbaboranes and ferrocene derivatives together with the specific features of the compounds themselves may be extremely attractive as objects of study from both theoretical and applied points of view.

The present review deals with the literature between 1965 and 1983.

## II. THE NOMENCLATURE, STRUCTURE, AND TYPES OF BONDING IN POLYHEDRAL BORON-CONTAINING SYSTEMS WITH THE CpFe FRAGMENT IN THE POLYHEDRON

The compounds described cannot always be conveniently named in accordance with IUPAC rules.[10] For this reason, the trivial nomenclature adopted in the literature will also be used. In many cases, names will be omitted and will be replaced by graphical representations of the molecules and their overall formulae.

The structure of ferracarbaboranes, ferraboranes, and ferraheteroboranes with a CpFe fragment is described satisfactorily by the corresponding polyhedra and is determined both by the number of atoms in the polyhedral skeleton and by the type of these atoms. The types of bonding in polyhedral boron-containing systems have been discussed in a number of communications.[8,11-14] The qualitative description of the bonds in a metallacarbaborane polyhedron can be briefly formulated in terms of the following items:

1. All the electrons in the metallacarbaborane molecule are delocalised along the surface of the polyhedron.

2. Each atom in the polyhedron provides three atomic orbitals (AO) for polyhedral bonding. For the boron and carbon atoms and the atoms of other elements in the First Period, there remains one AO for bonding with another ligand (for example, a hydrogen, carbon, etc. atom). After being bound in the polyhedron, the transition metal atoms have six unoccupied AO, which are used for bonding with other ligands ($C_5H_5$, CO, $PR_3$, etc.) or are occupied by electrons not involved in bonding and localised at the metal atom.

3. The number of bonding molecular orbitals (MO) in the closed polyhedra (the *closo*-structure) with $n$ vertices ($n \geq 5$) is $n + 1$. Consequently the number of skeletal electrons is $2n + 2$. The number of occupied MO is $n + 1$.

4. If the number of skeletal electrons in the polyhedron is greater than $2n + 2$, the latter acquires an open structure. When the number of electrons is $2n + 4$ we have the *nido*-structure (one vertex is lacking for the *closo*-structure). When the number of electrons is $2n + 6$, we have the *arachno*-structure (two vertices are lacking for the *closo*-structure). When the number of electrons is $2n + 8$, the *hypho*-structure obtains (three vertices are lacking for the *closo*-structure).

5. The *closo*-, *nido*-, *arachno*-, and *hypho*-metallacarbaboranes can be regarded as electronic analogues of the corresponding carbaboranes, boranes, and also carbaborane and borane anions.

Ferracarbaboranes and ferraboranes with the CpFe fragment in the polyhedron and having the *closo*- and

†Here and henceforth $\eta^5$-$C_5H_5Fe$ = CpFe.

*nido*-structures are widely known. The *arachno*- and *hypho*-metallacarbaboranes have been obtained comparatively recently[6] and only a few examples are known. The theory underlying the qualitative treatment of bonding in polyhedral boron- and metal-containing systems has been called the theory of the counting of skeletal electron pairs (TCSEP). It is also known in the literature as Wade's rule. In the course of further development of the chemistry of metallacarbaboranes, compounds have been obtained with a structure which could not be predicted on the basis of the TCSEP.[15-17] In addition, *closo*-ferracarbaboranes with one or several CpFe subunits and a polyhedral skeleton do not have a negative charge for the $d^5$ electronic configuration of the iron atom. Thus the total number of skeletal electrons is less than the number necessary for the *closo*-structure, the number of the missing electrons being equal to the number of the CpFe subunits in the polyhedron. The theory of bonding in the given system was developed further in the review of O'Neill and Wade.[18]

## III. GENERAL METHODS OF SYNTHESIS OF FERRACARBABORANES

Five main methods of synthesis of ferracarbaboranes, which are analogous to the general methods of synthesis of metallacarbaboranes, have been described in the literature:

1. Direct addition of the metal-containing group to the free boron-containing ligand, whereupon the ligand does not undergo structural changes.
2. Direct addition of the metal-containing group to the free boron-containing ligand in which the ligand undergoes marked structural changes.
3. Rearrangement or partial destruction of the metallacarbaborane with formation of a new complex.
4. Introduction of a boron atom into a metal complex with hydrocarbon ligands.
5. Introduction of a carbon atom into a metallaborane complex.

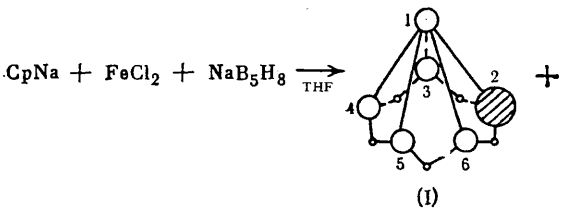
The first method of synthesis is very common. Numerous ferracarbaboranes with planar heterocyclic ligands, for example, borole, diborolin, thiadiborolin, borazine, etc. In addition, ferracarbaboranes with anionic carbaborane ligands, namely $C_2B_9H_{11}^{2-}$, $C_2B_{10}H_{12}^{2-}$, etc., have been obtained by this method. The second method of synthesis is also fairly widely known. One of the examples is the synthesis of ferracarbaboranes by the polyhedral expansion method. The third method of synthesis can be illustrated by various thermal rearrangements of the polyhedral skeleton and also by the polyhedral contraction reaction involving the ferracarbaborane nucleus. The fourth and fifth methods are so far known for only a limited number of examples, but they are undoubtedly promising and their development in the immediate future may be expected.

## IV. COMPOUNDS HAVING (6-11)-VERTEX POLYHEDRAL STRUCTURES

In the systematic description of various polyhedral complexes containing both boron and iron, the latter will be considered in terms of increasing numbers of vertices in the polyhedron.

### 1. 6-Vertex Polyhedra

Only a limited number of examples of compounds of this type are known and all the ferracarbaboranes and ferraboranes obtained have the *nido*-structure. The ferraborane $CpFeB_5H_{10}$ (I) was obtained in a low yield together with other products on interaction of CpNa with $FeCl_2$ and $NaB_5H_8$ in THF at 25 °C:[19,20]

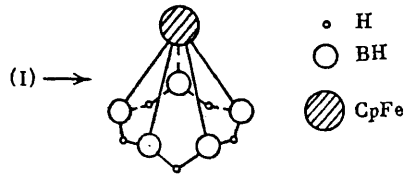



(I)

$$+ CpFeB_{10}H_{15} + Cp_2FeB_8H_8 .$$

H BH CpFe

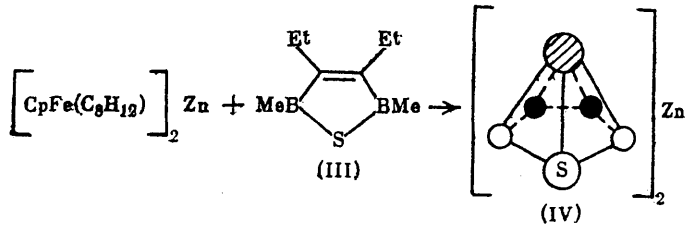
The structure of $Cp_2FeB_8H_8$ has not been established and the structure of $CpFeB_{10}H_{15}$ will be discussed below. On the basis of $^1H$ and $^{11}B$ NMR spectra, a pentagonal-pyramidal structure was assigned to complex (I). On heating in deuteriotoluene, the complex rearranges to the isomeric ferraborane (II), which is a structural analogue of ferrocene:




(II)

Like complex (I), the ferraborane (II) is a paramagnetic substance unstable in air.

On refluxing of the zinc salt of $\eta^5$-cyclopentadienyl-$\eta^4$-cycloocta-1,5-dienyliron in hexane with an excess of 3,4-diethyl-2,5-dimethylthiadiborolin (III), the zinc salt of the thiadiborolinyliron complex (IV) is obtained:[21]



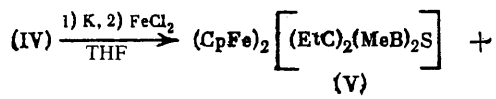

(III) (IV)

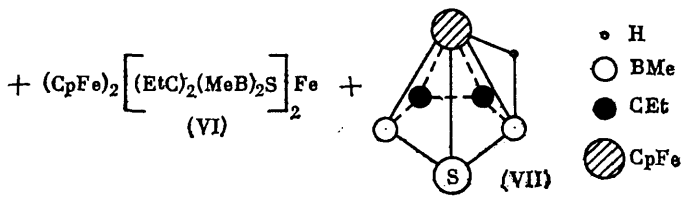
BMe CEt CpFe

Complex (IV) has 16 skeletal electrons, which are responsible for the *nido*-structure of its pentagonal pyramid#. The interaction of complex (IV) with potassium entails the replacement of the zinc cation by the potassium cation.

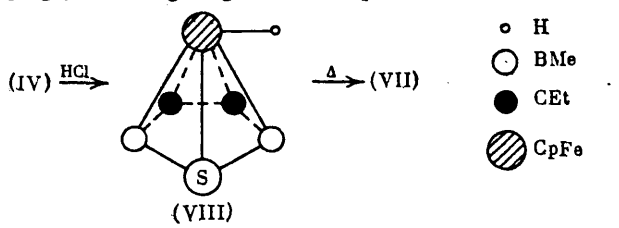
#Here and henceforth the number of skeletal electrons is calculated and its relation with the structure of the complexes considered established on the basis of the TCSEP.

The subsequent reaction with $FeCl_2$ in THF leads to the formation of a mixture of ferracarbaboranes:



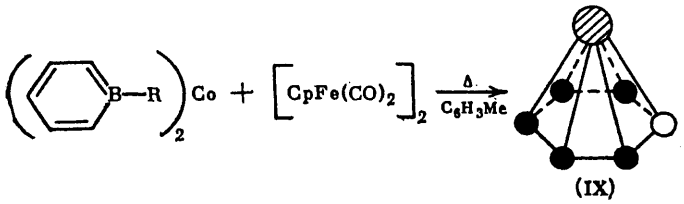



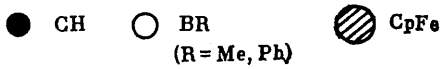

The structure of complexes (V) and (VI) will be examined below. Complex (VII), obtained in a very small amount, is isostructural with the initial complex (IV). Hydride hydrogen occupies the bridging position between the boron and iron atom, which has been demonstrated by $^{11}B$ NMR. Treatment of the zinc salt (IV) with dry HCl results in the formation of complex (VIII), containing a hydrogen atom linked to the Fe atom by a σ-bond. On heating of complex (VIII), the hydride hydrogen at the Fe atom passes to the bridging position, giving rise to complex (VII):



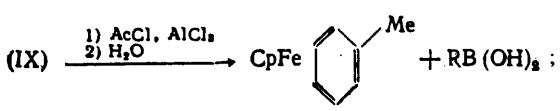

## 2. 7- and 8-Vertex Polydedra

The hexagonal-pyramidal derivatives of $\eta^6$-borarenyl-$\eta^5$-cyclopentadienyliron (IX) have been obtained by heating bis($\eta^6$-borarenyl)-cobalt with $[CpFe(CO)_2]_2$ in mesitylene:[22]



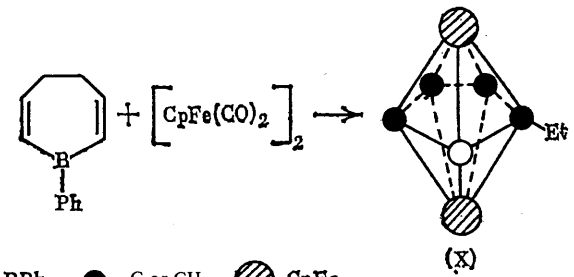




Complexes (IX) are crystalline substances stable in air. Their molecules contain 18 skeletal electrons and have the *nido*-structure. Oxidation of complex (IX) on treatment with $Ce^{4+}$ leads to the removal of the boron atom from the polyhedral skeleton and to the formation of the methyl- or phenyl-ferrocenium cation in a high yield. Acylation of complex (IX) with acetyl chloride under the conditions of the Friedel-Crafts reaction entails the replacement of the BR fragment in the borarene ligand by the CMe fragment:




R=Me; Ph.

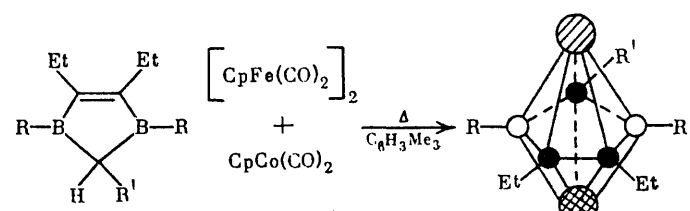
The above group of complexes is also of interest because it contains a large number of the so-called "multidecker sandwiches". Heating of 1-phenyl-4,5-dihydroborepin with $[CpFe(CO)_2]_2$ leads to the isomerisation of the boron-containing ligand and the formation of the diamagnetic complex (X), which is a triple-decker sandwich:[4]







Complex (X) contains 16 electrons and has the *closo*-structure, which has been demonstrated by X-ray diffraction (the Fe–Fe distance is 3.27 Å). When the alkyldiborolin (XIa) is heated with $[CpFe(CO)_2]_2$ and $CpCo(CO)_2$ at 180–200 °C in an inert atmosphere, the mixed diamagnetic complex (XIIa), containing Fe and Co atoms in the $d^6$ configuration, is formed in a low yield:[23]

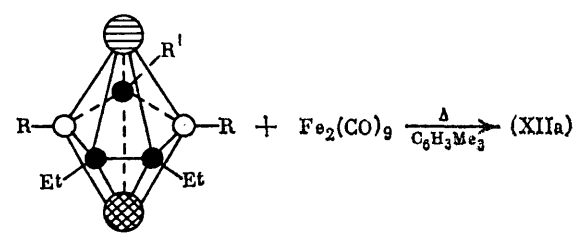



(XIa): R = Et, R' = Me
(XIb): R = Me, R' = H

(XIIa): R = Et, R' = Me
(XIIb): R = Me, R' = H




Complex (XIIa) is stable in air and can be sublimed *in vacuo* at 120 °C. Its *closo*-structure is due to the presence of 16 skeletal electrons. The synthesis of complex (XIIa) on heating the cobaltanickelacarbaborane (XIIIa) with iron nonacarbonyl in mesitylene has been described. Complex (XIIa) is then formed in a moderate yield (~10%) together with other metallocarbaboranes:[24]

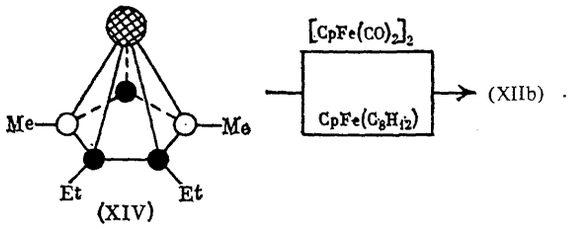


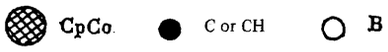

(XIIIa): R = Et, R' = Me
(XIIIb): R = Me, R' = H




Complex (XIIb) has been obtained in a moderate yield by the reaction of the cobaltacarbaborane (XIV) with organo-

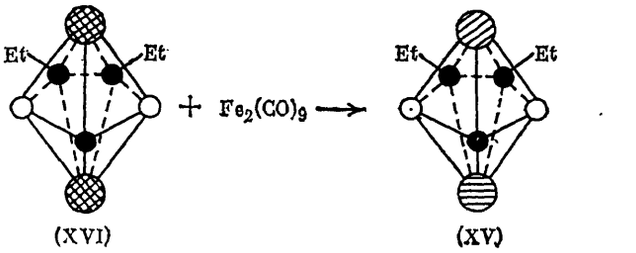
iron compounds:




The complex is formed in a very low yield together with other metallocarbaboranes when the cobaltacarbaborane (XIV) is reduced by potassium in THF, this being followed by reaction with $CpFe(CO)_2I$. Finally, complex (XIIb) has been obtained in a high yield by the reduction of the cobaltanickelcarbaborane (XIIIb) by potassium in THF and subsequent treatment with $FeCl_2$. It is believed[24] that complexes (XII, a and b) contain 30 valence electrons (in each case 6 $\pi$ electrons of the Cp rings, 6 *d* electrons of the Fe atom, 8*d* electrons of the Co atom, and 4$\pi$ electrons of the $C_3B_2$ ligand). Complex (XIIb) has the *closo*-structure, which has been demonstrated by X-ray diffraction (the bond distances are 3.104 Å for Fe–Co, 1.624 Å for Fe–$C_3B_2$, and 1.58 Å for Co–$C_3B_2$). On treatment with potassium in THF, complex (XIIb) is converted into a paramagnetic anion (31 valence electrons), while oxidation with $AgBF_4$ in ether results in the formation of the paramagnetic cation (29 valence electrons). According to EPR data, the maximum spin density in the anion is concentrated at the cobalt atom. On the basis of Mössbauer spectra, it is believed[24] that the structure of complex (XIIb) and its cation are related in the same way as the structures of ferrocene and the ferrocenium cation. The effective magnetic moments of the cation of complex (XIIb) ($\mu_{eff}$ = 2.10 $\mu_B$), its temperature dependence, and the potentials of the anion $\rightleftharpoons$ neutral complex $\rightleftharpoons$ cation reversible transitions have been measured. The above communication[24] quotes data obtained by quantum-chemical calculations for complexes (XII, a and b) carried out using the extended Hückel method; the energies of all the 17 highest occupied MO, the types of the MO, and the contributions by the AO of the metals were determined. It follows from the calculated data that the CpFe fragment is linked to the $C_3B_2$ ring more strongly than the CpCo fragment. The EPR, Mössbauer, and electrochemical data are consistent with the main conclusions drawn from the quantum-chemical calculation.

The dinuclear ferracarbaborane (XV), containing both the CpFe and $(CO)_3Fe$ fragments in the polyhedral skeleton, has been obtained by the reaction of the dinuclear nickelacarbaborane (XVI) with $Fe_2(CO)_9$:[24]

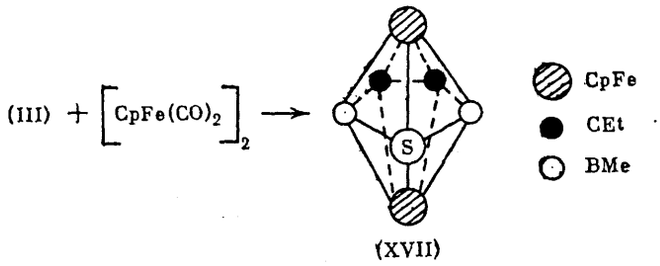




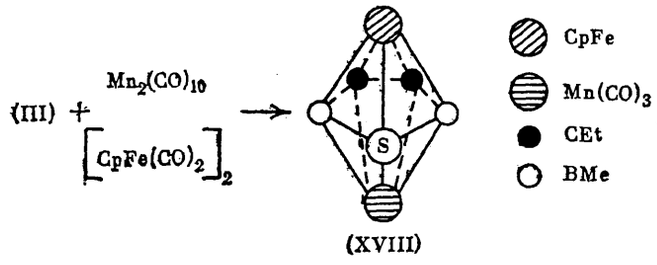


Complex (XV) is obtained in a mixture with other metallocarbaboranes, its maximum yield being obtained when the reaction is carried out in boiling mesitylene.

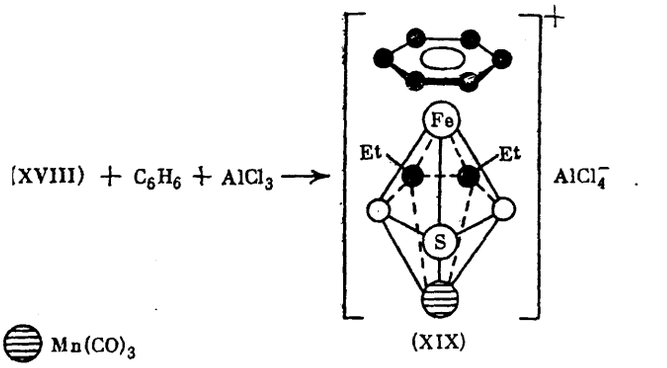
It is possible to obtain 7-vertex polyhedral ferracarbaboranes, containing an S atom in the polyhedron, by the reaction of thiadiborolin (III) with organic derivatives of transition metals (Fe, Co, Mn). The reaction with $[CpFe.(CO)_2]_2$ in boiling mesitylene affords a three-decker sandwich with two iron atoms—complex (XVII):[25]




The structure of this complex, which is a diamagnetic crystalline substance stable in air but decomposing on treatment with inorganic acids, has been demonstrated by X-ray diffraction. The $C_5H_5$ and $C_2B_2S$ rings are planar and have the transoid conformation, while the Fe–Fe distance is 3.236 Å. The interaction of the thiadiborolin (IV) with $[CpFe(CO)_2]_2$ and $Mn_2(CO)_{10}$ in boiling mesitylene leads to the formation of the diamagnetic complex (XVIII) with Fe and Mn atoms in the polyhedral skeleton:[26]




Complex (XVIII) is stable in air. Its *closo*-structure is determined by the presence of 16 skeletal electrons. Heating of complex (XVIII) in benzene in the presence of $AlCl_3$ results in the ready replacement of the Cp ligand by benzene:

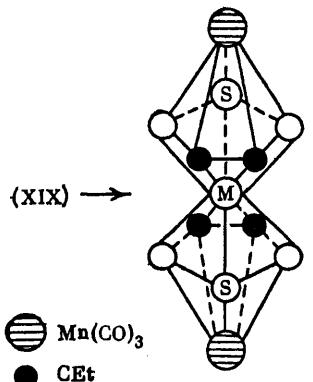






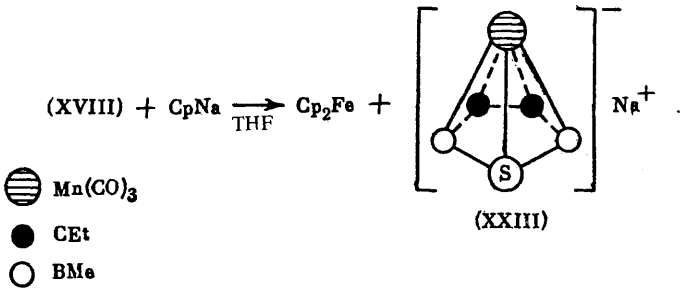
The cationic complex (XIX) formed under these conditions is extremely sensitive to hydrolysis. When it is heated *in vacuo*, a low yield of the mixed complex (XX), containing

3 metal atoms, is obtained:




(XX): M = Fe
(XXI): M = Co
(XXII): M = Ni

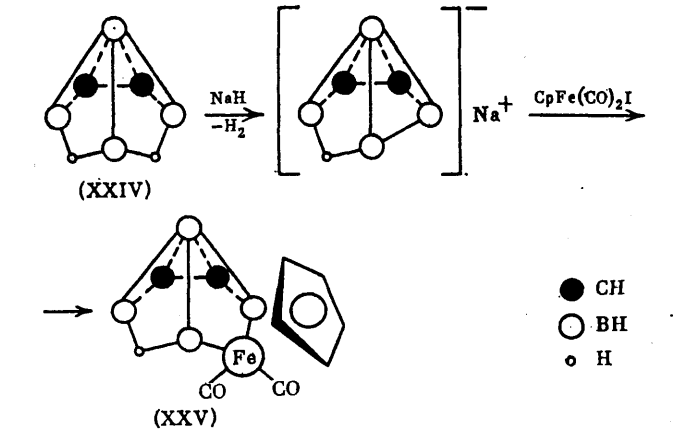
Another more general method of synthesis of complex (XX) and its structural analogues consists in treating complex (XVIII) with CpNa in THF.[27] This results in the removal of the CpFe fragment and the formation of the anionic complex (XXIII):




(XXIII)

Without being isolated, complex (XXIII) was made to react with transition metal chlorides of the type $MCl_2$ (M = Fe, Co or Ni) to form the trinuclear complexes (XX)–(XXII).

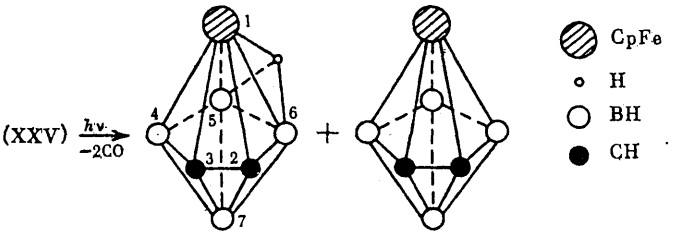
Another pathway leading to the synthesis of 7-vertex polyhedral *closo*-ferracarbaboranes involves the introduction of the CpFe fragment into the polyhedral skeleton of a *nido*-carbaborane. When the *nido*-carbaborane (XXIV) was treated with NaH in THF and then with $CpFe(CO)_2I$, the *nido*-carbaborane (XXV), which is sensitive to air and contains an Fe atom in a bridging position, was isolated in a satisfactory yield:[28,29]




(XXIV)

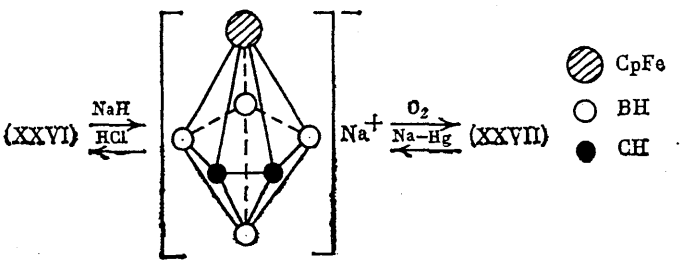
(XXV)

Irradiation of complex (XXV) with ultraviolet light leads to an almost quantitative yield of a mixture of the ferracarbaboranes (XXVI) and (XXVII):



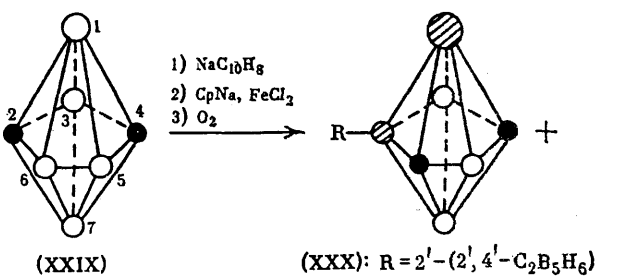

(XXVI) (XXVII)

Complex (XXVI) is diamagnetic (the Fe atom has the $d^6$ configuration) and contains 16 skeletal electrons, which determine its *closo*-structure, while complex (XXVII) is paramagnetic ($\mu_{eff}$ = 2.1 $\mu_B$ $d^5$ configuration of the Fe atom) and contains 15 skeletal electrons, i.e. is electron deficient. The reversible interconversion of the ferracarbaboranes (XXVI) and (XXVII) proceeds via the anionic complex (XXVIII) in accordance with the following mechanism:



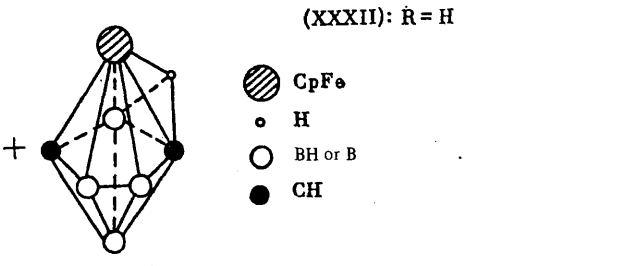

(XXVIII)

The substitution of the boron atom in the 1-position by the CpFe fragment and the formation of a mixture of the ferracarbaboranes (XXX)–(XXXIII) in a low yield via the mechanism




(XXIX)

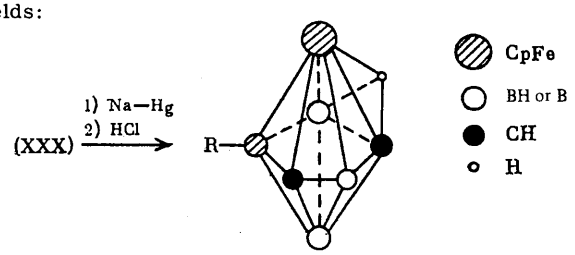
(XXX): R = 2′-(2′,4′-$C_2B_5H_6$)
(XXXI): R = $C_{10}H_7$
(XXXII): R = H




(XXXIII)

have been observed in the reaction of the *closo*-carbaborane 2,4-$C_2B_5H_7$ (XXIX) with sodionaphthalene and then with CpNa and $FeCl_2$.[29] Complexes (XXX)–(XXXII) are para-

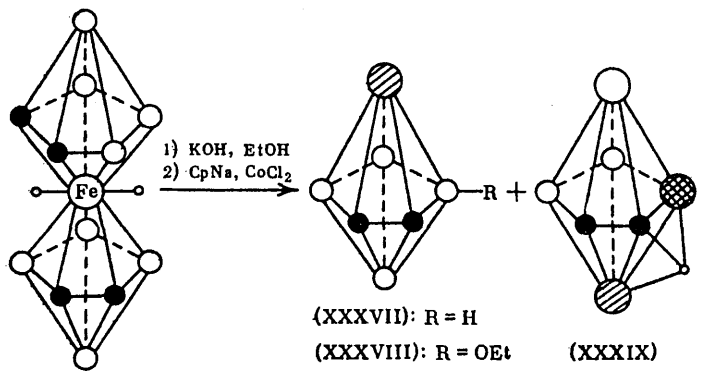
magnetic, while complex (XXXIII) is diamagnetic. Like the ferracarbaborane (XXVII), complex (XXX) is reduced by sodium amalgam to a diamagnetic derivative, whose protonation results in the formation of the diamagnetic complexes (XXXIV) and (XXXV) in overall quantitative yields:




(XXXIV): R = $2^1$-($2^1$,$4^1$-$C_2B_5H_6$)

(XXXV): R = H

Yet another method of synthesis of 7-vertex *closo*-ferracarbaboranes consists in the rearrangement of the *commo*-ferracarbaborane (XXXVI) on alkaline degradation and subsequent interaction with CpNa and $CoCl_2$.[30] The formation of a complex mixture of products, the main components of which were the ferracarbaboranes (XXXVII) and (XXXVIII), was then observed:

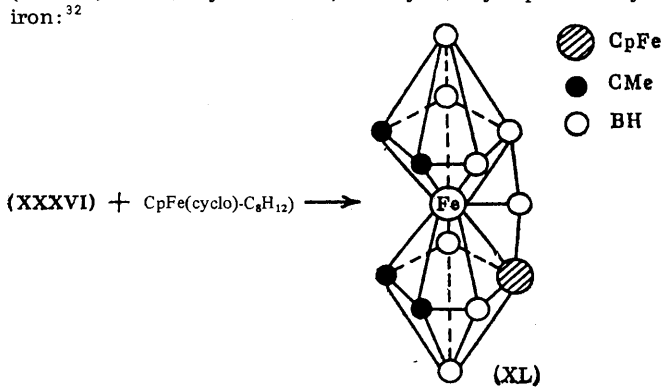






The ferracarbaboranes (XXXVII) and (XXXVIII) are paramagnetic, while the ferracobaltacarbaborane (XXXIX) is diamagnetic. Its structure was established by X-ray diffraction, from which it follows that it has the *closo*-structure. The Fe—Co distance is 2.56 Å.[31]

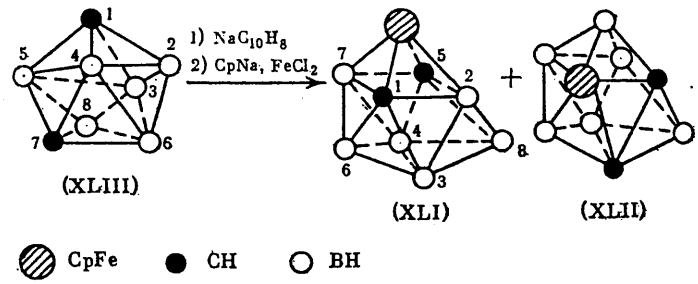
Only one example of an 8-vertex *closo*-ferracarbaborane with the CpFe fragment in the polyhedral skeleton is so far known. It was obtained from the *commo*-ferracarbaborane (XXXVI) and $\eta^4$-cyclo-octa-1,5-dienyl-$\eta^5$-cyclopentadienyl-iron:[32]




Complex (XI) consists, as it were, of two polyhedra joined together, namely the upper 7-vertex and lower 8-vertex polyhedra respectively. According to the TCSEP, the upper polyhedron lacks one skeletal electron and the lower polyhedron lacks two such electrons. Such a deficiency of skeletal electrons leads to a marked distortion of the geometry of the ferracarbaborane molecule, expressed by the "sharing" of the BH fragment by the upper and lower clusters. If two electrons could be in some way introduced into the skeleton of complex (XL), then it is believed[32] that it would acquire the normal geometry. The upper polyhedron would still remain a pentagonal bipyramid, while the lower polyhedron would be converted into a dodecahedron. It has been suggested[32] that the metallacarbaboranes whose polyhedral skeleton lacks two and more electrons be called hyperelectron-deficient.

### 3. Complexes Having the Structure of (9—11)-Vertex Polyhedra

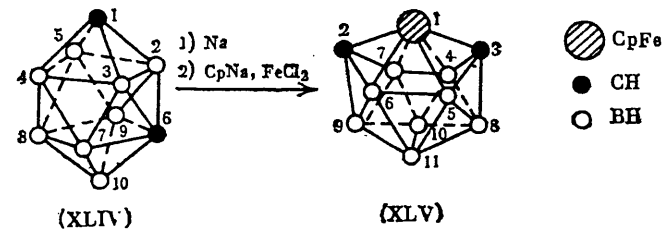
Two isomeric 9-vertex paramagnetic ferracarbaboranes (XLI) and (XLII), having the *closo*-structure and being represented by a three-cap trigonal prism, have been obtained by the polyhedral expansion of the *closo*-carbaborane 1,7-$C_2B_6H_8$ (XLIII):[33]





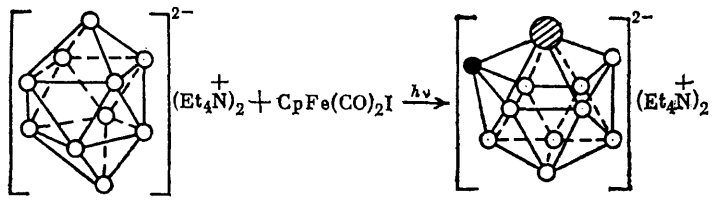


The polyhedral expansion of the *closo*-carbaborane 1,6-$C_2B_8H_{10}$ (XLIV) led to a satisfactory yield of the 11-vertex paramagnetic *closo*-ferracarbaborane (XLV):[33]




The ferracarbaboranes (XLI), (XLII), and (XLV) are readily reduced to the diamagnetic Fe(II)-forms by sodium amalgam. The dipole moments $\mu_{eff}$ have been measured[34] for the paramagnetic complexes (XLI), (XLII), and (XLV). Analysis of the EPR and $^{13}C$ and $^{11}B$ NMR spectra showed that the unpaired electron is localised not only at the Fe atom but also at the B and C atoms coordinating the metal atoms. The photochemical reaction of $(Et_4\overset{+}{N})_2B_{10}H_{10}^{2-}$ (XLVI) with $CpFe(CO)_2$ entails the polyhedral expansion of the borane skeleton with formation of the paramagnetic complex (XLVII), which is isostructural with complex

(XLV):[35]

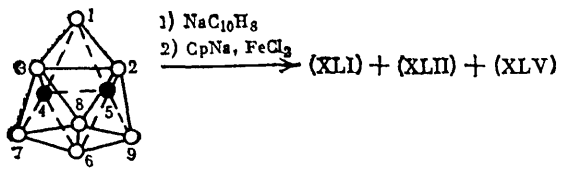



(XLVI) (XLVII)

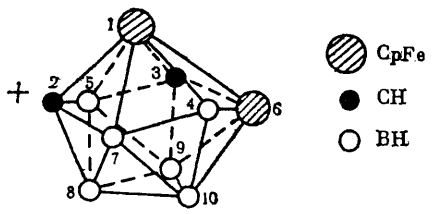
CpFe ● CH ○ BH

Complex (XLVII) has also been obtained on refluxing a solution of $K_2^+B_{10}H_{10}^{2-}$ and $CpFe(CO)_2I$ in 1,2-dimethoxyethane.

Structural distortions of the polyhedral skeleton in the electron-deficient dinuclear ferracarbaboranes is illustrated in relation to complex (XLVIII), which has been obtained, together with the ferracarbaboranes (XLI), (XLII) and (XLV), on polyhedral expansion of the *closo*-carbaborane $4,5\text{-}C_2B_7H_9$ (XLIX):[36]



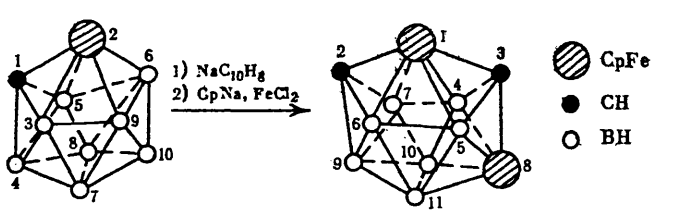

(XLIX)




(XLVIII)

The ferracarbaborane (XLVIII) is a paramagnetic substance ($\mu_{eff}$ = 3.05 $\mu_B$), but it is converted in the course of a week at 20 °C into a diamagnetic isomeric form, which can be explained by the reorientation, over a period of time, of the spins of the unpaired electrons from parallel to antiparallel.[36] The structure of complex (XLVIII) was established by X-ray diffraction, from which it follows that it is a distorted two-cap Archimedes antiprism. It has one "superfluous" bond between the Fe atom at the vertex and the Fe atom in the nearest tetragonal belt. The Fe–Fe distance is 2.57 Å. The distortion of the geometry of this complex has also been discussed by Nishimura.[37]

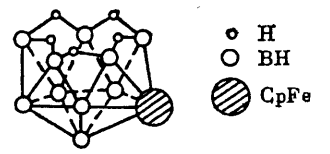
The polyhedral expansion of the *closo*-cobaltacarbaborane (L) results in the formation of the 11-vertex *closo*-ferracobaltacarbaborane (LI):[38]




(L) (LI)

Complex (LI) is a paramagnetic substance ($\mu_{eff}$ = 1.85 $\mu_B$), whose *closo*-structure has been demonstrated by X-ray diffraction.[39]

The ferraborane (LII) having the structure of the 11-vertex *nido*-polyhedron, obtained from $B_5H_8^-Na^+$, $FeCl_2$ and CpNa in a mixture with other ferraboranes, is an icosahedron from which one vertex has been removed:[20]

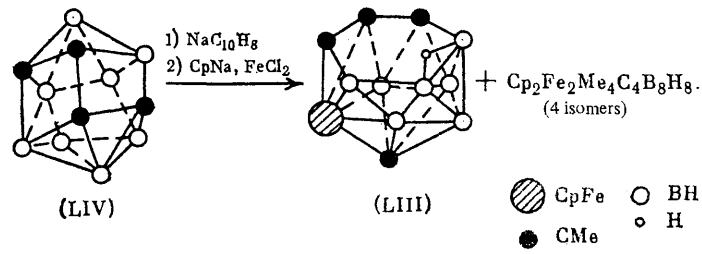



(LII)

Complex (LII) is diamagnetic, contains 26 skeletal electrons, and, in conformity with the TCSEP, has the *nido*-structure.

## V. COMPOUNDS HAVING 12-VERTEX POLYHEDRAL STRUCTURES

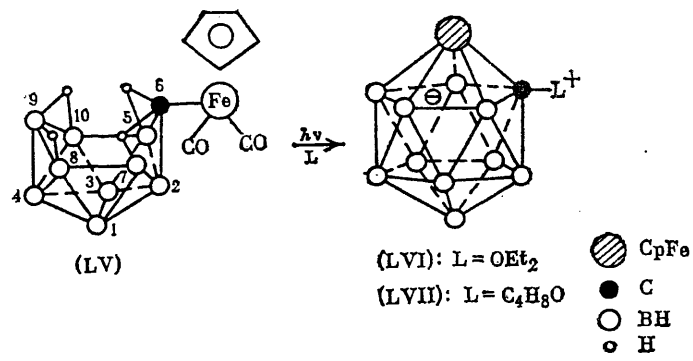
The 12-vertex *closo*-polyhedra have the icosahedral structure, while the *nido*-polyhedra have the structure of an "open" icosahedron with an open hexagonal face. The *nido*-ferracarbaborane (LIII), having 12 vertices, has been obtained, together with other products, on polyhedral expansion of the four-carbon *nido*-carbaborane $C_4Me_4B_8H_8$ (LIV):[40]




(LIV) (LIII)

The structure of complex (LIII) has been established by X-ray diffraction. The distances between the Fe atom and the C and B atoms to which it is coordinated are in the range 2.051–2.168 Å. Complex (LIII) is diamagnetic and contains 28 skeletal electrons, which give rise to its *nido*-structure in conformity with the TCSEP. The structures of the remaining products of this reaction will be discussed below.

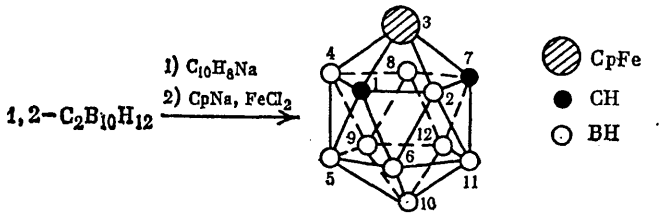
Irradiation of the σ-complex $B_{10}H_{13}$–σ-$Fe(CO)_2Cp$ (LV) with ultraviolet light in solution in ether or THF results in the "closure" of the polyhedral skeleton and the formation of a one-carbon ferracarbaborane (LVI) and (LXVII):[41]




(LV)

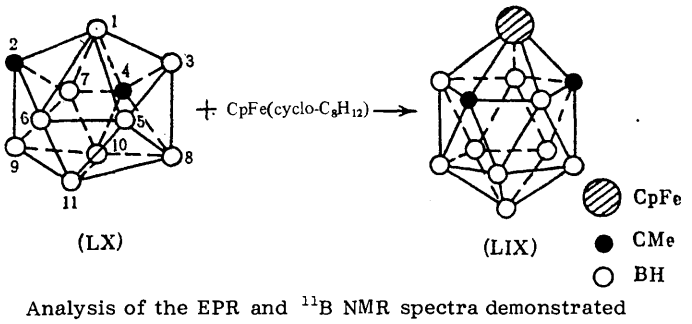
Complexes (LVI) and (LVII) each contain 25 skeletal electrons, i.e. one less than required by the TCSEP for the icosahedral *closo*-structure. Both complexes are isoelectronic with the ferrocenium cation. The *closo*-structure of complex (LVI) has been confirmed by X-ray diffraction.

The paramagnetic ferracarbaborane (LVIII), containing C atoms in the *meta*-positions relative to one another, has been obtained in a low yield together with other products on polyhedral expansion of *o*-carbaborane:[42]



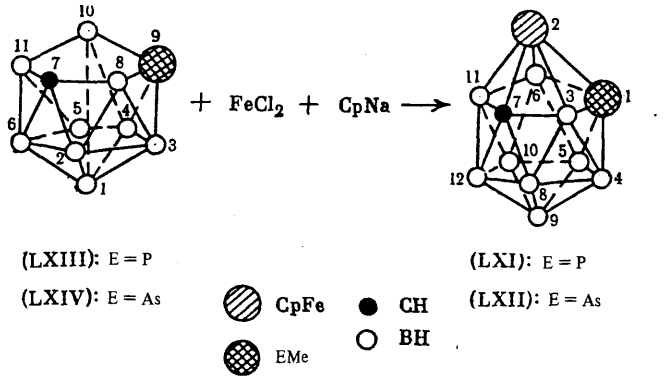

(LVIII)

Another method of synthesis of the 1,7-dimethylferracarbaborane (LIX), an analogue of complex (LVIII), based on the polyhedral expansion of the *closo*-carbaborane 2,3-$Me_2$-2,3-$C_2B_9H_9$ (LX) in its reaction with $\eta^4$-cyclo-octa-1,5-dienyl-$\eta^5$-cyclopentadienyliron, was discovered later:[43]




(LX) (LIX)

Analysis of the EPR and $^{11}B$ NMR spectra demonstrated the delocalisation of the spin density of the unpaired electron over the C(1), C(7), B(2), B(4), and B(8) atoms. The dipole moments $\mu_{eff}$ of complex (LVIII) have been measured.[44] The icosahedral ferraphosphacarbaborane (LXI)[35] and ferra-arsacarbaborane (LXII)[45] have been obtained by the reaction of the *nido*-phosphacarbaborane (LXIII) in THF and the *nido*-arsacarbaborane (LXIV) in $Et_3N$ respectively with $FeCl_3$ and CpNa:




(LXIII): E = P
(LXIV): E = As
(LXI): E = P
(LXII): E = As

Both complexes, (LXI) and (LXII), are diamagnetic and each contains 26 skeletal electrons, which give rise to their *closo*-structures.

The polyhedral expansion of the 11-vertex *closo*-ferracarbaborane (XLV) results in the formation of the 12-vertex paramagnetic complex (LXV) containing two CpFe fragments:[46]

$$(XLV) \xrightarrow[2)\ [CpFeC_8H_8]^+]{1)\ NaC_{10}H_8} Cp_2Fe_2C_2B_8H_{10}$$

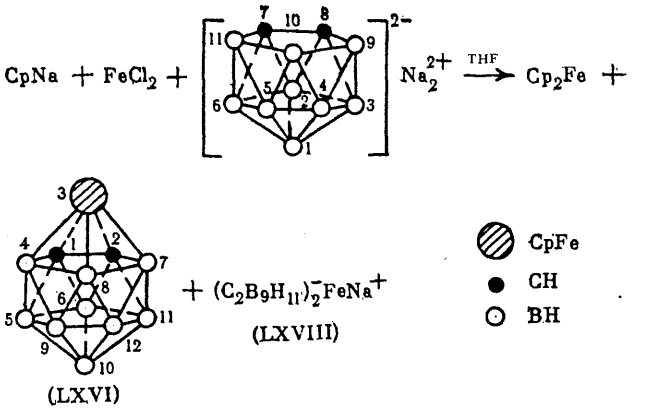
(LXV)

The structure of complex (LXV) has not been established. On standing for several days, it decomposes with reformation of the initial complex (XLV).

## VI. THE MOST IMPORTANT 12-VERTEX *CLOSO*-FERRACARBABORANE—$\eta^5$-CYCLOPENTADIENYL-$\eta^5$-(3)-1,2-DICARBOLLYLIRON

### 1. Synthesis and Physical Properties

The ferracarbaborane investigated in greatest detail among the icosahedral complexes is $\eta^5$-cyclopentadienyl-$\eta^5$-(3)-1,2-dicarbollyliron (LXVI), which was first obtained in a moderate yield by the interaction of CpNa, $FeCl_2$, and 7,8-$C_2B_9H_{11}Na_2$ (LXVII) in THF:[47,48]




(LXVI) (LXVIII)

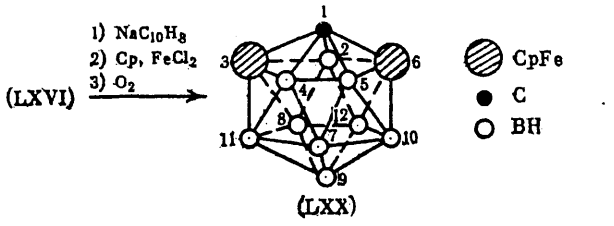
Ferrocene and the *commo*-ferracarbaborane (LXIII) is then formed together with compound (LXVI). A more convenient method of synthesis of compound (LXVI), based on the reaction of *o*-carbaborane, cyclopentadiene, and $FeCl_2$ with methanolic alkali and subsequent treatment of the reaction mixture with $H_2O_2$, has been proposed.[49] Compound (LXVI) is a purple paramagnetic substance and constitutes an electronic analogue of the ferrocenium cation, i.e. its Fe atom has the $d^5$ configuration. The structure of compound (LXVI) has been established.[50] The complex is a regular icosahedron in which the Fe atom is equidistant from the C and B atoms coordinating it, its distance from these atoms amounting to ~2.07 Å. It has 25 skeletal electrons, i.e. one less than is necessary for the 12-vertex *closo*-polyhedron—the icosahedron.

When compound (LXVI) is treated with sodium amalgam in acetonitrile, the diamagnetic monoanion [3-Cp-3,1,2-$FeC_2B_9H_{11}]^-$ (LXIX), isoelectronic with ferrocene (the Fe atom has the $d^6$ configuration), is formed.[47,48] Complex (LXIX) contains 26 skeletal electrons, which fully satisfies the TCSEP requirements for icosahedral *closo*-structures. The study of the kinetics of the oxidation of the Fe(III)-form of compound (LXVI) to the Fe(II)-form (LXIX) showed that the oxidation mechanism is analogous to that of the oxidation of ferrocene to the ferrocenium cation.[51] The EPR spectra of complex (LXVI) revealed the presence of an unpaired electron.[52] Analysis of the EPR and $^{11}B$ NMR spectra demonstrated the localisation of the spin density in complex (LXVI) at the B and C

atoms coordinating the Fe atom.[34] The experimental value of $\mu_{eff}$ for complex (LXVI)[34,53] proved to be close to the calculated value.[54] The study of the Mössbauer spectra of this compound showed that its quadrupolar splitting parameters are close to the corresponding values for the biscyclopentadienyl complexes, although they are somewhat higher than the latter.[55,56] The cause of this consists in the higher density of *s* electrons at the Fe atom than in the ferrocene–ferrocenium derivatives, indicating a more effective removal of *d* electrons from the Fe atom in compound (LXVI) owing to their involvement in $\pi$ bonding with the ligands. Quantum-chemical calculation for the Fe(II)-form (LXIX) by the MO method with adjustment for self-consistency with respect to the atomic charges and atomic configurations showed that the Fe–$C_2B_9H_{11}$ interaction involves mainly the ligand $\sigma$ orbitals, while the Fe–$C_5H_5$ interaction involves the $\pi$ orbitals of the Cp ring.[57] Calculation of the total atomic charges showed that the maximum negative charge is present on the B(8) atom located symmetrically in the open $C_2B_3$ face of the dicarbollyl ligand, while the maximum positive charge is localised at the B(10) atom most remote from the Fe atom. In addition, it has been shown that the HOMO of complex (LXIX) has appreciable $d_{z^2}$ character, as in ferrocene.

## 2. The Chemical Properties of $\eta^5$-Cyclopentadienyl-$\eta^5$-(3)-1,2-Dicarbolyliron and Its Derivatives

The chemical properties and reactivity of compound (LXVI) and its derivatives have been investigated in greatest detail compared with other ferracarbaboranes. On polyhedral expansion of the Fe(III)-form (LXVI), the dinuclear complex (LXX) was obtained in a very small amount together with 13-vertex ferracarbaboranes. The regular icosahedral structure was attributed to compound (LXX) on the basis of $^{11}B$ NMR spectra:[46]



(LXX)

Although both Fe atoms in complex (LXX) have the $d^5$ configuration, the complex is diamagnetic, which can be accounted for by the antiparallel orientation of the unpaired electron spins at the metal atoms. Complex (LXX) contains 24 skeletal electrons—two less than is required by the TCSEP for icosahedral *closo*-structures, which is characteristic of ferracarbaboranes containing several Fe atoms. The formation of complex (LXX) can be explained by the presence in the reaction medium of traces of NaOH under the influence of which complex (LXVI) undergoes initially alkaline degradation with removal of the B(6) atom from the polyhedral skeleton and its subsequent replacement by the CpFe fragment.

A detailed investigation of the chemical properties of compound (LXVI) and its derivatives has been undertaken by the authors of this review[58–68] and is considered below.

*(a) Reactions of compound (LXVI) with electrophiles.* In order to study the distribution of the relative electron density, the bromination of compound (LXVI)§ and of its bromo-derivatives was investigated.[58] It was shown that complex (LXVI) is brominated stepwise at the B atoms of the dicarbollyl ligand. In the absence of a catalyst, the first bromine atom enters the 8-position, while further bromination takes place only in the presence of $AlCl_3$ in the 9- and 12-positions:

$$(\text{LXVI}) \xrightarrow{Br_2} \underset{(\text{LXXI})}{CpFeC_2H_2B_9H_8\text{-}8\text{-}Br} \xrightarrow[AlCl_3]{1)\ Br_2} \underset{(\text{LXXII})}{CpFeC_2H_2B_9H_7\text{-}8,9\text{-}Br_2}$$

$$\xrightarrow[AlCl_3]{2)\ Br_2} \underset{(\text{LXXIII})}{CpFeC_2H_2B_9H_6\text{-}8,9,12\text{-}Br_3} .$$

The structure of the bromo-derivatives (LXXI)–(LXXIII) was demonstrated by $^{11}B$ NMR and also by specific synthesis from the bromo-derivatives (LXXIV) and (LXXV), where the bromine atoms are known to be in the 9- and 9- and 12-positions:

$$\underset{(\text{LXXIV})}{CpFeC_2H_2B_9H_8\text{-}9\text{-}Br} \xrightarrow{Br_2} (\text{LXXII}) ;$$

$$\underset{(\text{LXXV})}{CpFeC_2H_2B_9H_7\text{-}9,12\text{-}Br_2} \xrightarrow[AlCl_3]{Br_2} (\text{LXXIII}) .$$

The bromination of the 4-bromo-derivative (LXXVI) leads to the 4,8-dibromo-derivative (LXXVII):

$$\underset{(\text{LXXVI})}{CpFeC_2H_2B_9H_8\text{-}4\text{-}Br} \xrightarrow{Br_2} \underset{(\text{LXXVII})}{CpFeC_2H_2B_9H_7\text{-}4,8\text{-}Br_2} .$$

The presence of bromine atoms in compound (LXVI) makes it less reactive in electrophilic substitution reactions. It follows from the bromination data that the distribution of relative electron density in the dicarbollyl ligand of compound (LXVI) is as follows: B(8) > B(9), B(12) > B(4), B(5), B(6), B(10), B(11), C(1), C(2).

When compound (LXVI) is treated with thallium(III) trifluoroacetate in trifluoroacetic acid, the B–H bond is oxidised and the 8-trifluoroacetoxy-derivative (LXVIII) is formed:[59]

$$(\text{LXVI}) \xrightarrow[CF_3COOH]{Tl(OCOCF_3)_3} \underset{(\text{LXXVIII})}{CpFeC_2H_2B_9H_8\text{-}8\text{-}OCOCF_3} .$$

The structure of complex (LXXVIII) has been established by X-ray diffraction. Its methanolysis affords the 8-hydroxy-derivative (LXXIX):

$$(\text{LXXVIII}) \xrightarrow{H^+,\ MeOH} \underset{(\text{LXXIX})}{CpFeC_2H_2B_9H_8\text{-}8\text{-}OH} .$$

The oxidation of the B–H bond when compound (LXVI) is treated with $Tl(OCOCF_3)_3$ indicates an enhanced hydride mobility of the H atom at the B(8) atom.

Mercuration of compound (LXVI) by mercury(II) trifluoroacetate in the $CF_3COOH$–$CH_2Cl_2$ mixture yielded the 9-chloromercuri-derivative (LXXX):[60]

$$(\text{LXVI}) \xrightarrow[2)\ NaCl]{1)\ Hg(OCOCF_3)_2} \underset{(\text{LXXX})}{CpFeC_2H_2B_9H_9\text{-}9\text{-}HgCl} .$$

§ $CpFeC_2H_2B_9H_9$ and $CpFeHCB_9H_9CH$ are two ways of writing the formula of compound (LXVI) ($d^5$ configuration of the Fe atom).

When it is treated with bromine, the 9-bromo-derivative (LXXIV) is produced.

*(b) Derivatives of compound (LXVI) substituted at a C atom of the dicarbollyl ligand.* The synthesis of derivatives of compound (LXVI) substituted at a C atom of the dicarbollyl ligand and their subsequent reactions have been described.[61–63] These derivatives have been synthesised from the corresponding 1-substituted o-carbaboranes, cyclopentadiene, and $FeCl_2$ in methanolic alkali:

$$o\text{-}HCB_{10}H_{10}C\text{-}R + C_5H_6 + FeCl_2 \xrightarrow[2)\ H_2O_2]{1)\ KOH,\ MeOH} CpFeHCB_9H_9C\text{-}R;$$

$$R=CH_2OH,\ CH=CH_2,\ \overset{CH_3}{\underset{|}{C}}=CH_2,\ C\equiv CH,\ CH_2OH.$$

In order to synthesise the acid (R = COOH), 7-COOH-7,8-$C_2B_9H_{11}K$ was used as the starting material. The proposed methods of synthesis of derivatives of compound (LXVI) with a functional group at a C atom of the dicarbollyl ligand make them readily available, which made it possible to investigate various reactions of 1-substituted ferracarbaboranes. Together with the usual properties of the carbaborane and cobaltacarbaboranes analogues, these reactions manifest specific features due to the presence of the ferracarbaborane nucleus. Various reactions of the hydroxymethyl derivative $CpFeHCB_9H_9CH_2OH$, namely acylation, oxidation to the aldehyde, and replacement of the OH group by OR or Cl under the conditions of acid catalysis, have been investigated.[61] The solvolysis of the chloromethyl derivative $CpFeHCB_9H_9CCH_2Cl$, which demonstrated the ability of the $CpFe^{III}HCB_9H_9C$ group to stabilise as the intermediate species the carbonium ion centre linked to it, has been investigated. The synthesis of a ketone, secondary carbinols, and the diethyl acetal of an aldehyde derived from compound (LXVI) has been described. The ability of compound (LXVI) to form hydrogen bonds with basic solvents involving the C–H bonds of both ligands has been demonstrated by infrared spectroscopy[64] and the acid character of the C–H bonds of the dicarbollyl ligand in compound (LXVI) has been confirmed,[61] since they are metallated on treatment with butyl-lithium in ether. The ionisation constants of the acids $CpFeHCB_9H_9CCOOH$ in 50% ethanol ($pK_a$ = 3.49) and $CpFeHCB_9H_9CCH_2COOH$ in 80% methylcellosolve ($pK_a$ = 5.70) have been measured. The induction constant for the $CpFe^{III}HCB_9H_9C$ group ($\sigma_i$ = 0.31) was calculated from the latter $pK_a$ by Charton's method, from which it follows that the ferra(III)carbaboranyl group exhibits an appreciable electron-accepting effect.[61] The majority of the reactions of the 1-substituted derivatives of compound (LXVI) described can be used as preparative methods for their synthesis. The conversion of the Fe(III)-form into the Fe(II)-form of the 1-substituted derivatives of compound (LXVI) has been suggested[63] and consists in reduction by $NaBH_4$ in ethanol:

$$CpFeHCB_9H_9C\text{—}R \xrightarrow[2)\ CtX]{1)\ NaBH_4} [CpFe^{II}HCB_9H_9C\text{—}R]\,Kt;$$

$$R=CH_2OH,\ CH(OH)CH_3,\ CH=CH_2,\ C(CH_3)=CH_2,\ C\equiv CH;$$

$$Ct=Cs,\ Me_4N;$$

$$X=Cl,\ Br,\ I,\ NO_3.$$

The derivatives of the Fe(II)-form of compound (LXVI) are electronic analogues of ferrocene.

*(c) Carbonium ions stabilised by the ferra(II)carbaboranyl group.* The authors of the present review investigated the carbonium ion centre linked to the $CpFe^{II}HCB_9H_9C^-$ group[63,65] and found that the group stabilises the carbonium ion linked to it much more effectively than the ferrocenyl group. Since the positive charge on the carbon atom is balanced by the negative charge on the ferra(II)carbaboranyl group, the cation-containing molecule is electrically neutral and therefore exists in the form of zwitter-ions. Such zwitter-ions have been called[63,65] carbenium zwitter-ions. The protonation of the carbinols (LXXXI), (LXXXII), and (LXXXIII) by inorganic acids gave high yields of the primary carbenium zwitter-ion (LXXXIV) and the corresponding secondary zwitter-ions (LXXXV) and (LXXXVI) respectively:

$$[CpFe^{II}HCB_9H_9C\underset{\underset{OH}{|}}{\text{—}CHR}]^- \xrightarrow{H^+} CpFe^{II}HCB_9H_9C^-\text{—}C^+\!\!<^{R}_{H}$$

(LXXXI): R=H
(LXXXII): R=Me
(LXXXIII): R=Ph

(LXXXIV): R=H
(LXXXV): R=Me
(LXXXVI): R=Ph

A convenient method of synthesis of the secondary and tertiary carbenium zwitter-ions, (LXXXV) and (LXXXVII) respectively, consists in the protonation of the corresponding olefins (LXXXVIII) and (LXXXIX):

$$[CpFe^{II}HCB_9H_9C\underset{\underset{R}{|}}{\text{—}C=CH_2}]^- \xrightarrow{H^+} CpFeHCB_9H_9\bar{C}\text{—}\overset{+}{C}\!\!<^{Me}_{R}$$

(LXXXVIII): R=H
(LXXXIX): R=Me

(LXXXV): R=H
(LXXXVII): R=Me

The carbenium zwitter-ions (LXXXIV) and (LXXXVII) have been isolated in an individual form. They are diamagnetic, stable in air, and capable of being chromatographed on silica gel in moderately polar eluents. The relative stabilities on prolonged storage in air of the carbenium zwitter-ions increase in the sequence $\overset{+}{C}H_2 \ll \overset{+}{C}HMe \ll \overset{+}{C}HPh \cong \overset{+}{C}Me_2$. Conclusions about the structure and the probable mechanism of the stabilisation of the carbonium ion centre in such systems were reached from the X-ray diffraction analysis of the phenylcarbenium zwitter-ion (LXXXVI). The carbonium ion centre is stabilised by the strong iron-carbon interaction [the Fe–$C^+$ distance is 2.23 Å and the angle between the C(carbaborane)–$C^+$ bond and the $C_2B_3$ plane is 47°].

Furthermore, the $C^+$ atom has the $sp^2$-configuration and the C(carbaborane)–$C^+$ distance is 1.38 Å, from which follows the partial double bond character of the linkage between the $C^+$ atom and the carbon atom of the polyhedron. Thus the carbonium ion centre is stabilised in two ways—both by the electron-donating effect of the ligand with formation of a fulvene-like structure and with participation of the Fe atom.

Various reactions of the carbenium zwitter-ions have been investigated.[63,65] Despite their lower reactivity compared with organic carbonium ions and ferrocenyl carbonium ions, they combine with bases via the carbonium ion centre. The reactions of the primary and secondary zwitter-ions, (LXXIV) and (LXXXV) respectively, with electrically neutral Lewis bases lead to the formation of

adducts in the form of inner salts of type (XC):

$$(LXXXIV) \text{ or } (LXXXV) \xrightarrow{L} CpFe^{II}HCB_9H_9C\text{-}\overset{R}{\overset{|}{C}}H\text{-}\overset{+}{L}\ ;$$

(XC)

R=H or Me, L=$PPh_3$, $NC_5H_5$, $SMe_2$, N≡C—Me, N≡C—CH=$CH_2$.

The acid hydrolysis of the acetonitrilium inner salt (XC, R = H, L = N≡CMe) with simultaneous oxidation by $H_2O_2$ leads to the formation of the *N*-substituted acetamide $CpFeHCB_9H_9CCH_2NHCOMe$. The reaction of the tertiary zwitter-ion (LXXXVII) with pyridine leads to the adduct (XCI) and the olefin (LXXXIX) as the deprotonation product.

$$(LXXXVII) \xrightarrow{C_5H_5N} CpFe^{II}HCB_9H_9\bar{C}—CMe_2—\overset{+}{N}C_5H_5 + (LXXXIX).$$

The primary and secondary zwitter-ions, (LXXXIV) and (LXXXV) respectively, react with organolithium compounds, combining with the organic residue via the carbonium ion centre with formation of products of type (XCII):

$$(LXXXIV) \text{ or } (LXXXV) \xrightarrow[2)\ H_2O_2]{1)\ R'Li} CpFeHCB_9H_9C—CH\begin{matrix}R\\R'\end{matrix};$$

(XCII)

R=H or Me; R'=Bu, Ph, Bu—C≡C, Ph—C≡C, 1,2-$C_2B_{10}H_9$-1.

The reaction of the primary and secondary zwitter-ions with nucleophilic anions takes place similarly, affording products of type (XCIII):

$$(LXXXIV) \text{ or } (LXXXV) \xrightarrow[2)\ H_2O_2]{1)\ Nu^-} CpFeHCB_9H_9C—CH\begin{matrix}R\\Nu\end{matrix};$$

(XCIII)

R=H or Me; Nu=CN, iso-BuO, iso-BuS, PhO, PhS, $CH_2NO_2$.

On the other hand, cyanide and thiophenoxide anions do not add to the tertiary zwitter-ion (LXXXVII) and only the deprotonation of one of the methyl groups takes place with formation of the alkene (LXXXIX), which indicates an increased acidity of the H atoms of the methyl group in the tertiary and zwitter-ion. The primary and tertiary zwitter-ions, (LXXXIV) and (LXXXVII) respectively, abstract a hydride ion from $NaBH_4$, which leads to the quantitative formation of the methyl derivative (XCIV) and the isopropenyl derivative (XCV) respectively of complex (LXVI):

$$(LXXXIV) \text{ or } (LXXXVII) \xrightarrow[2)\ H_2O_2]{1)\ NaBH_4} CpFeHCB_9H_9C—CHR_2.$$

(XCIV): R=H
(XCV): R=Me

In contrast to this, when the primary zwitter-ion (LXXXIV) is treated with $H_2AlCl$ in ether, the diethyloxonium inner salt (XCVI), which is extremely resistant to hydrolysis, is formed:

$$(LXXXIV) \xrightarrow{H_2AlCl,\ Et_2O} CpFe^{II}HCB_9H_9\bar{C}CH_2\overset{+}{O}Et_2.$$

(XCVI)

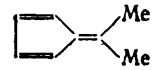
In the absence of $H_2AlCl$, the cation (LXXXIV) does not react with ether even after prolonged heating. The more basic dimethoxyethane adds to the cationic centre of the primary zwitter-ion, giving rise to the inner salt (XCVII):

$$(LXXXIV) + MeOCH_2CH_2OMe \rightarrow CpFe^{II}HCB_9H_9\bar{C}\text{-}CH_2\overset{+}{\underset{|}{O}}\text{-}CH_2CH_2OMe.$$

Me

(XCVII)

The stabilisation of the carbonium ion centre linked to the $HCB_9H_9CHFe^{II}C_5H_4$ group has been investigated.[66] The isopropenyl derivative (XCVIII), containing a substituent in the Cp ring, has been obtained in order to synthesise this carbonium ion system from 6,6-dimethylfulvene, the 7,8-dicarbollide anion (LXVII), and $FeCl_2$ in the liquid ammonia–THF mixture:



$$+ (LXVII) + FeCl_2 \xrightarrow[2)\ H_2O_2]{1)\ NaNH_2} \rightarrow CH_2=\overset{Me}{\overset{|}{C}}—C_5H_4FeHCB_9H_9CH.$$

(XCVIII)

Complex (XCVIII) was reduced to the diamagnetic form (XCIX) with sodium tetrahydroborate:

$$(XCVIII) \xrightarrow[2)\ Me_4NBr]{1)\ NaBH_4} Me_4N[CH_2=\overset{Me}{\overset{|}{C}}—C_5H_4FeHCB_9H_9CH].$$

(XCIX)

The protonation of the alkene (XCIX) leads to the formation of a carbenium zwitter-ion (C), which was not isolated in an individual state owing to its high reactivity:

$$(XCIX) \xrightarrow{H^+} \{Me_2\overset{+}{C}C_5H_4Fe^{II}HCB_9H_9\bar{C}H\}.$$

(C)

In solution the cation (C) and the cationic component of (C) undergo a series of reactions. If the protonation is carried out in benzene, only the dimeric product (CI), which is a result of the addition of the cationic component of (C) to the double bond of the alkene (XCIX), is obtained:

$$(XCIX) \xrightarrow{H^+} \{(C)\} \xrightarrow[-H^+]{(XCIX),\ O_2} \rightarrow HCB_9H_9CHFeC_5H_4—CMe_2—CH=\overset{Me}{\overset{|}{C}}—C_5H_4FeHCB_9H_9CH.$$

(CI)

If its protonation is carried out in ether or dimethyl sulphide, then the inner salts (CII) and (CIII) are obtained together with the dimeric complex (CI):

$$(XCIX) \xrightarrow{H^+,L} L^+—CMe_2—C_5H_4Fe^{II}HCB_9H_9\bar{C}H + (CI).$$

(CII): L=$OEt_2$
(CIII): L=$SMe_2$

In the case of dimethyl sulphide, an appreciable amount of the inner salt having the dimeric structure (CIV) is formed in addition to complexes (CIII) and (CI):

$$HCB_9H_9CHFeC_5H_4—CMe_2—\overset{Me}{\overset{|}{\underset{|}{C}}}—C_5H_4Fe^{II}HCB_9H_9\bar{C}H.$$

$^+SMe_2$

(CIV)

It follows from these data that the carbonium ion centre is stabilised less effectively by the $HCB_9H_9CHFe^{II}C_5H_4$ group than by the $CpFe^{II}HCB_9H_9C$ group.

The greater stabilising capacity of the $CpFe^{II}HCB_9H_9\bar{C}$ group made it possible to obtain the stable vinyl cation (CV) and to isolate it for the first time in an individual state in the form of the zwitter-ion on protonation of the alkyne derivative (CVI):[66,68]

$$\underset{\text{(CVI)}}{[CpFe^{II}HCB_9H_9C{-}C{\equiv}CH]^-} \xrightarrow{H^+} \underset{\text{(CV)}}{CpFe^{II}HCB_9H_9\bar{C}{-}\overset{+}{C}{=}CH_2}.$$

The vinyl cation (CV) is diamagnetic and stable in air. it combines eith hydrogen halides via the vinyl cationic group to form tertiary carbenium zwitter-ions of type (CVII) in which the halogen atom is linked directly to the carbonium ion centre:

$$\text{(CV)} \xrightarrow{HX} CpFe^{II}HCB_9H_9\bar{C}{-}\overset{+}{C}\begin{matrix}\nearrow Me\\ \searrow X\end{matrix}.$$

(CVII): X=Cl, Br

When the vinyl cation (CV) is treated with nucleophiles, for example $NaBH_4$ or MeLi, only the deprotonation of the vinyl cationic group takes place with formation of the alkyne (CVI), while the products of the addition to the cationic centre, namely the alkenes (LXXXVIII) or (LXXXIX), are obtained in extremely small amounts. These data indicate the appreciable acidity of the hydrogen atoms in the vinyl cationic group.

The allyl cation system, stabilised by the $CpFe^{II}HCB_9H_9\bar{C}$ group, has also been investigated.[67] When the aldehyde (CVIII) is treated with β-styrylmagnesium bromide, the phenylallyl cation (CIX) is formed in the form of the zwitter-ion:

$$\underset{\text{(CVIII)}}{CpFeHCB_9H_9CCHO} \xrightarrow{PhCH{=}CHMgBr} \longrightarrow \underset{\text{(CIX)}}{CpFe^{II}HCB_9H_9\bar{C}{-}CH{=}\overset{+}{C}H{-}CHPh}.$$

The monosubstituted allyl cation (CX) was obtained analogously for the first time from the aldehyde (CVIII) and vinylmagnesium bromide:

$$\text{(CVIII)} \xrightarrow[2)\ H^+]{1)\ CH{=}CH_2MgBr} \underset{\text{(CX)}}{CpFe^{II}HCB_9H_9\bar{C}{-}CH{=}\overset{+}{C}H{-}CH_2}.$$

Both allyl cations, (CIX) and (CX), exhibit the dual reactivity characteristic of allyl cationic systems. The addition of the hydride ion entails the formation of the corresponding allyl derivative (CXI) and the *n*-propenyl derivative (CXII) of compound (XIVI):

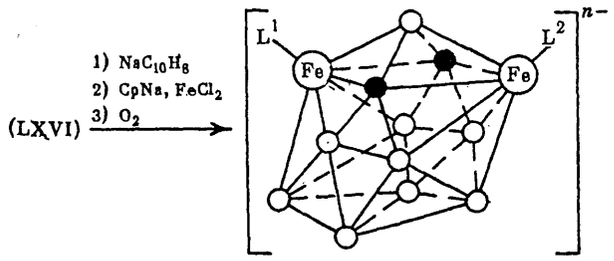
$$\text{(CIX) or (CX)} \xrightarrow{NaBH_4} \underset{\text{(CXII)}}{[CpFe^{II}HCB_9H_9C{-}CH_2{-}CH{=}CHR]^- + [CpFe^{II}HCB_9H_9C{-}CH{=}CH{-}CH_2R]^-}.$$

The stability of the carbonium ions stabilised by the ferra(II)carbaboranyl group have no analogy in the chemistry of both organic and organometallic carbonium ions. All the above features suggest that these are carbonium ions of a new type. Furthermore, the above reactions of the carbonium ions can be regarded as a convenient preparative method for the synthesis of various derivatives of compound (LXVI).

## VII. COMPOUNDS HAVING 13- AND 14-VERTEX POLYHEDRAL STRUCTURES

### 1. 13-Vertex Polyhedral Ferracarbaboranes

The *nido*-ferracarbaboranes containing 13 vertices are so far unknown. The *closo*-polyhedron with 13 vertices is an icosahedron containing an additional vertex. Polyhedral expansion of compound (LXVI) yielded as the main product the diamagnetic dinuclear ferracarbaborane (CXIII).[60] The diemagnetic dinuclear complex (CXIV) was obtained in a much smaller amount at the same time:




(CXIII): $L^1 = L^2 = Cp$; $n = 0$

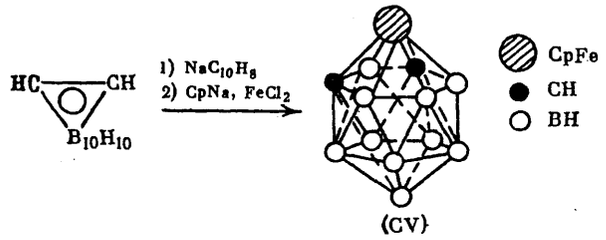
(CXIV): $L^1 = Cp$; $n = 1$

$L^2 = \eta^5$-1,2-$C_2B_9H_{11}$

● CH
○ BH

Preliminary X-ray diffraction analysis of complex (CXIII) demonstrated the absence of the Fe–Fe bond (3.2 Å). Structures have been attributed to complexes (CXIII) and (CXIV) on the basis of $^{11}B$ NMR spectra. Both Fe atoms in each complex have the $d^5$ configuration. Each complex has 26 skeletal electrons, i.e. according to the TCSEP they are electron-deficient. Their diamagnetism is due to the antiparallel orientation of the spins of the unpaired electrons, which arises in their conjugation with the π orbitals of the carbaborane ligand.

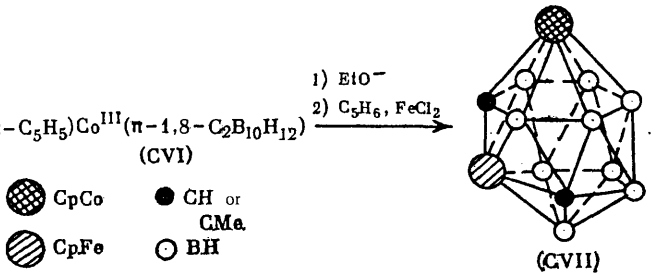
The main product of the polyhedral expansion reaction of o-carbaborane is complex (CV), which has the *closo*-structure:[42]




(CV)

The complex is paramagnetic and its reduction with $NaBH_4$ leads to a diamagnetic monoanion, which has been isolated in the form of the tetramethylammonium salt $[CpFe^{II}C_2B_{10}H_{12}]\cdot NMe_4$. The latter compound contains 28 skeletal electrons, which establish, according to the TCSEP, its *closo*-structure. The alkaline degradation of the 13-vertex *closo*-cobaltacarbaborane (CVI) entails the removal of the B(5) atom. The subsequent reaction with cyclopentadiene and $FeCl_2$ leads to the introduction of the CpFe fragment in the 5-position and the formation of the paramagnetic dinuclear *closo*-

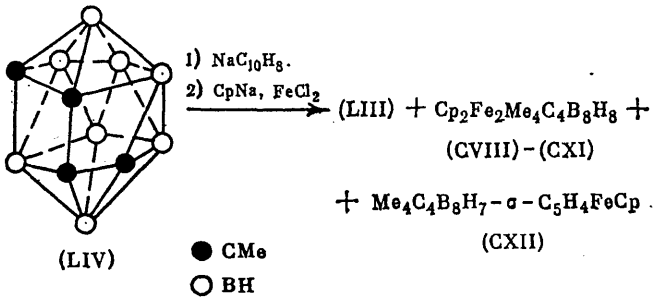
cobaltaferracarbaborane (CVII):[38,69]



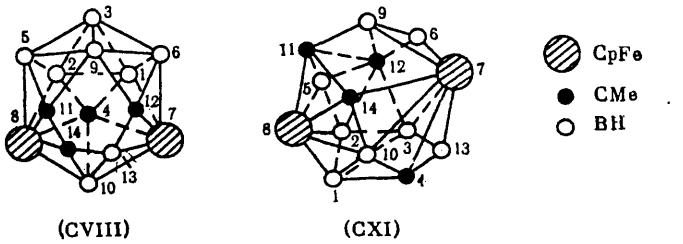

On treatment with $NaBH_4$, complex (CVII) is reduced to the diamagnetic monoanion [4-CpCo-5-CpFe$^{II}$-1,8-$C_2B_9H_{11}$]$^-$.

## 2. 14-Vertex Polyhedral Ferracarbaboranes

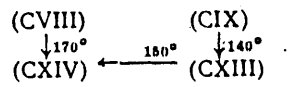
The 14-vertex *closo*-polyhedra can have structures of two types—those of a two-cap hexagonal antiprism and a six-cap cube. The 14-vertex *nido*-polyhedra can exist in several structures with a pentagonal or tetragonal open face. Polyhedral ferracarbaboranes with 14 vertices have been obtained comparatively recently and for this reason only a few examples are so far known. The polyhedral expansion of the four carbon *nido*-carbaborane (LIV) with subsequent addition of the CpFe fragment leads to the formation of a complex mixture of products containing 14-vertex dinuclear ferracarbaboranes:[40,70-73]



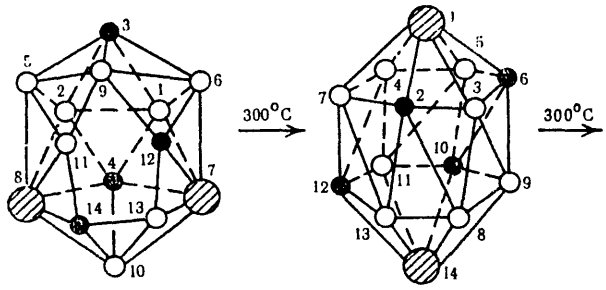

Compound (CXII) is a four-carbon carbaborane substituted at the B atom by the ferrocenyl group, which has been demonstrated by X-ray diffraction.[73] The dinuclear ferracarbaboranes (CVIII)–(CXI) have been obtained in the form of four diamagnetic isomers. The structures of complexes (CX) and (CXI) have not so far been established. Those of the isomers (CVIII) and (CIX) have been determined by X-ray diffraction.[70,71] Both complexes have the *nido*-structure with pentagonal B(9)–C(11)–C(14)–B(13)–B(12) [compound (CVIII)] and tetragonal Fe(7)–C(14)–C(11)–B(9) [compound (CIX)] openfaces. A mechanism has been proposed for the formation of several ferracarbaboranes of different structure from one four-carbon carbaborane, namely compound (LIV).[72]

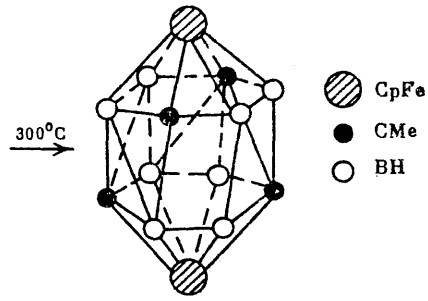



The ferracarbaboranes (CVIII) and (CIX) each contain 30 skeletal electrons and, according to the TCSEP, should have the *closo*-structure, which is not in fact observed. This can be accounted for by the presence of an appreciable potential barrier to the transition from the 14-vertex *nido*-systems to *closo*-systems.[71] On heating in nonane, the *nido*-ferracarbaboranes (CVIII) and (CIX) rearrange:




The structure of complex (CXIII) has not been established, while the diamagnetic complex (CXIV) has been characterised by X-ray diffraction.[71] The ferracarbaborane has the *nido*-structure with an open pentagonal face. On further heating, complex (CXIV) isomerises to the *closo*-polyhedron (CXV), which is also capable of undergoing thermal rearrangement to complex (CXVI):




Complexes (CXV) and (CXVI) are diamagnetic and each contains 30 skeletal electrons, which satisfies the TCSEP requirement for 14-vertex polyhedral *closo*-structures. The structures of complexes (CXV) and (CXVI) have been proposed on the basis of the analysis of their $^{11}B$ and $^{13}C$ NMR spectra.[71] Thus the isomeric ferracarbaboranes (CVIII), (CIX), and (CXIV) are a new class of metallacarbaboranes—metallacarbaboranes which have the *nido*-structure although the *closo*-structure is preferred. They have been called pseudo-*nido*-metallacarbaboranes.[71] The greater stability of the 14-vertex dinuclear ferracarbaboranes when the CpFe fragments in the polyhedral skeleton are separated from one another to the maximum extent as a consequence of the maximum overlap of the AO between individual vertices of the polyhedron has been justified theoretically.[74] It has been suggested that the pseudo-*nido*-ferracarbaboranes be regarded as precursors of the hitherto unknown polyhedral *closo*-metallacarbaboranes with 15 vertices.[71] Thus if a CpCo fragment coordinated to the atoms of the pentagonal open face could be introduced in some way into complexes (CVIII) and (CXIV),

one could obtain 15-vertex polyhedral *closo*-cobaltferracarbaborane of the type $CoFe_2C_4B_8$, satisfying the TCSEP requirements—32 skeletal electrons for 15 vertices.

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As can be seen from the data described above, the efforts of investigators of polyhedral ferracarbaboranes, ferraboranes, and ferraheteroboranes with the CpFe fragment in the skeleton have been largely concentrated on the development of methods for the synthesis of new polyhedral systems, while the chemistry of these interesting compounds remains, with a small exception, virtually uninvestigated. The study of the reaction of one of the ferracarbaboranes, namely $\eta^5$-cyclopentadienyl-$\eta^5$-(3)-1,2-dicarbollyliron, and of its derivatives yielded a number of interesting compounds with unusual properties. In view of the wide variety of ferracarbaborane systems, we are justified in assuming that these will be found to undergo new interesting chemical reactions.

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# Reaction-sorption Methods for the Concentration of Impurities in Their Gas-chromatographic Determination in Air

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The role of the reaction-sorption (chemical-sorption) method in the analysis of contaminants in air is examined, the physicochemical principles of the method are briefly described, and examples of their practical use for the identification and quantitative determination of harmful impurities in the atmosphere and in the air of the workplace in factories are presented. The review is based on studies published in 1972-1985.
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## I. INTRODUCTION

The successful struggle against the contaminaton of air, water, and soil by harmful chemical compounds, mainly of anthropogenic origin, often depends on the development of effective methods for the monitoring of toxic chemicals, among which gas chromatography has quite justifiably received most attention, particularly in the analysis of volatile organic compounds.[1-5] The first studies on the gas-chromatographic determination of harmful substances in the atmosphere and in the air of the workplace in factories were published about 25 years ago and at the present time ~80% of all the determinations of organic compounds in air are made by this method.[2,3,5] The develoment of gas-chromatographic methods and the expansion of their applications have continued up to the present time[6-11] and combined or hybrid methods have been acquiring increasing importance.[3,4,6] In our view, the greatest advances in the development, improvement, unification, and wide-scale employment of chromatographic methods for the monitoring of contaminants in air can be expected on these lines.[1-4,12-14]

Together with the use of physical methods,[3,4,14] the combination of chemical and chromatographic methods has been used successfully in gas chromatography for the identification of the separated substances.[6] The chemical methods in gas chromatography are based on the use of the chromatographic separation of impurities in combination with chemical reactions of the eluate.[3,6,9] The simplicity and effectiveness of the chemical methods[6] have gained for them a well established place in the analytical chemistry of the contaminants of air, particularly in the selective gas-chromatographic determination of the most important (target) components of the contamination[3,9] and for the identification of minor components in complex mixtures of harmful substances.[3,10,11] Analytical reaction gas chromatography includes three methods: the separation method (chromatography), the method used to determine the compounds analysed (physicochemical detection), and the method for the chemical transformation of the compounds analysed.[6]

This review is devoted to the use of one of the most important versions of the gas-chromatographic analysis of impurities—the reaction-sorption method (RSM), which includes the concentration, identification, and quantitative determination of harmful substances in air.

## II. THE APPLICATION OF REACTION-CHROMATOGRAPHIC METHODS IN THE DETERMINATION OF CONTAMINANTS IN AIR

The most important problem in the analytical chemistry of the contaminants in air is that of the correct and reliable identification of volatile toxic substances after their chromatographic separation.[3] The determination of the qualitative chemical composition of a sample of complex and multicomponent mixtures of different nature is known to be extremely difficult and the validity of the analysis depends on many factors and in the first place on the method used to identify the mixture components.[4,10,14]

The traditional methods for identification from the chromatographic retention characteristics of the impurities[14] (the method of additives, the use of pure substances, the application of logarithmic relations between the retention volume or index and the properties of the compound analysed, etc.) make it possible to achieve reliable results only in the analysis of mixtures of known or partly known composition or mixtures of substances of one homologous series (class, type).[2-4] In more complex cases, in the analysis of compounds of several types, these methods are as a rule relatively ineffective and either chromatographic samples on columns with stationary liquid phases of different polarity, or analysis with the aid of selective detectors, or reaction-chromatographic determination (identification) of impurities are used in order to obtain reliable results.[2,3,5]

However, the identification of chromatographic spectra obtained on columns with different types of packing involves highly significant difficulties and, when selective detectors are used (for example, an electron capture or flame ionisation detector), the information obtained is not always unambiguous owing to the lack of information about the sensitivity of these detectors for compounds of different classes.[3]

In all cases of the analysis of complex mixturs of impurities in air the reaction-chromatographic methods for the identification of impurities, which make it possible to achieve significantly more reliable results than the standard chromatographic procedures, are more effective.[2,3,5,10,11] In the analysis of mixtures of inorganic compounds it is much easier to identify the impurities than to elucidate the complex chromatographic spectra of organic substances, which as

a rule correspond to many isotypical compounds with similar properties.[3,4] In the determination of inorganic substances, one therefore is more likely to be concerned with the improvement of the detection characteristics, the reduction of the limits of detection of impurities, and the increase in the selectivity of the determinations against the background of other compounds in the sample accompanying the determination or interfering with the latter.[3,9]

One of the most effective and simplest reaction-chromatographic procedures for the identification of impurities is the subtraction (absorption) method.[6] Its principle consists in the absorption of individual compounds or separate groups (classes) of chemical substances in a reactor placed in the chromatograph thermostat before or after the chromatographic column.[6,8] The combination of the methods for the subtraction of impurities with subsequent gas-chromatographic analysis of the eluate with the aid of selective detectors[6,10,11] or the combination of the reaction-chromatographic methods with the usual gas-chromatographic analytical procedures[3,5,6,9] is even more effective.

However, one extremely significant disadvantage is characteristic of all the methods listed above. When all the impurities present in air are concentrated simultaneously in the trap with the sorbent, the subsequent identification of the compounds is made very much more difficult and in addition there is an appreciable change in the composition of the sample (and the results of the analysis are therefore distorted) as a result of the chemical reactions of the test substances on contact with the adsorbent[3,11,14] or in the extraction of the sample from the trap by the thermal desorption method.[8]

The fractionating sampling method, which makes it possible to avoid the above difficulties and significantly increases the reliability of the idenfitication of impurities, is therefore much more promising.[2,5,8,11–13] One way of solving this problem involves the use in gas chromatography of the method of the reaction-sorption concentration of impurities.

## III. THE REACTION-SORPTION METHOD—A NEW VERSION OF THE PROCEDURE FOR THE CONCENTRATION OF IMPURITIES IN ANALYSIS

### 1. Concentration of Impurities on Solid Sorbents

Analysis of the literature in recent years,[1–13] devoted to the determination of contaminants in air, has shown that in all these publications special attention has been devoted to questions of sampling and concentration of microimpurities. This is not fortuitous. Sampling is one of the most difficult stages in the analytial procedure for the determination of impurities in air. The results of exact and careful analysis lose all significance when the sample is incorrectly taken and when the sampling procedure is invalid.[3] This is particularly relevant to the analysis of contaminants in air—a complex labile system containing a multiplicity of chemical compounds with low concentrations and subjected to the action of moisture, oxidants, radiation, etc.

Analytical chemists have nowadays concentrated attention on the problem of obtaining a representative sample of the contaminants in air, whose components differ markedly from one another in their chemical and physical properties and in their concentrations (from $10^{-4}$ to $10^{-7}$ wt.%).[3,9–11] This question is extemely important because, having entered the concentrator, the compounds of the sample pass to a completely diffierent state:[3,5,7,14] (1) the concentration of impurities increases appreciably (by a factor of 100–1000 or more); (2) substances with completely different chemical properties and concentrations (differing by factors of $10–10^8$), many of which are reactive, unstable, susceptible to oxidation, and tending to hydrolyse and to undergo other reactions, accumulate simultaneously in the trap with the sorbent; (3) the increase of the concentration of the impurities in the trap tends to increase the likelihood of chemical interactions and irreversible transformations of the sample components; (4) the active centres on the large surface area of the sorbent (and sometimes also the possible impurities in the sorbent, for example, metals) have a catalytic effect, accelerating these reactions; (5) during the enrichment of the sample on the sorbent, accompanying impurities are coadsorbed (competitively sorbed), which leads to anomalies in the saturation of the sorbent surface and the initial sample composition is distorted.

As a result of these processes, the concentrations of the impurities in the trap-concentrator with the sorbent become markedly differentiated. The adsorption of impurities takes place non-uniformly, as a result of which the quantitative composition of the concentrated impurities may differ greatly from their composition in air.[3,15,16] Furthermore, the chemical reactions of the sample in the trap alter its qualitative composition and distort the analytical results.[3,13,14]

Thus amines tend to interact specifically with free vinyl groups on the surface of Chromosorb 102 and Porapak Q.[17] The presence of traces of $O_2$ in the carrier gas (nitrogen) during the concentration of amine impurities from air and on raising the temperature of the sorbent in thermal desorption to 100 °C leads to the depolymerisation and oxidation of the sorbent.[18] As a result, false peaks ("artefacts") of aromatic ketones and other carbonyl compounds appear on the chromatograms, distorting the results of the identification of the impurity. The same sorbents interact vigorously with $NO_2$, forming NO at 25 °C, and, on raising the temperature (to 125 °C), NO and $H_2O$ are formed with simultaneous nitration of the polymeric sorbents.[19]

The sorption capacities of Tenax and Amberlite HAD-2 in relation to n-pentane, benzene, acetone, 2-propanol, and acetonitrile change significantly as a result of the nitration and sulphonation of the sorbent by the chemically active components of industrial waste (sulphur and nitrogen oxides), the maximum change in the sorbent capacity having been noted for polar sorbates.[20] All reactive gases ($Cl_2$, HCl, HBr, $ClF_3$, $F_2$, HF, $ClO_2$, $O_3$, $SO_2$, $SO_3$, $NO_2$, etc.) behave similarly, interacting with one another and with almost all known sorbents and connecting tubes of the chromatographic system.[21]

In the course of the trapping of smoke gases from air, Tenax is gradually decomposed by $NO_2$ and $SO_2$ with formation of 2,6-diphenyl-*p*-benzoquinone.[22] On sorbents such as activated charcoal, $Al_2O_3$, silica gel, Florisil, and Tenax, nitrosamines, which are initially absent from air, are formed when air is passed through them.[23] When impurities from air containing olefinic hydrocarbons and free halogens are concentrated on the surface of Tenax, Amberlites, and carbonaceous sorbents, chemical reactions take place (for example, the interaction of $Cl_2$ with but-2-ene or cyclohexene) and lead to the appearance in the mixture analysed of halogenohydrocarbons which were previously absent from it.[24]

The possibility of the appearance of false peaks during the sampling process is illustrated by the data in Table 1. By concentrating ethylbenzene, 1-hydroxyethylbenzene, acetophenone, 1-octanol, and 1-octanal from ozonised air (the $O_3$ content was 1.0–1.3 mg $m^3$) on Tenax, it was shown[25] that at room temperature these compounds are not oxidised in the column with Tenax. However, the simultaneous presence of

oxidants ($O_3$, $NO_2$, $SO_2$, $Cl_2$) and water vapour in air leads to the decomposition of Tenax and of the toluene, styrene, and cyclohexane microimpurities concentrated on it.[26] Several deuteriated oxidation, halogenation, and nitrosation products (three chlorostyrene isomers, benzaldehyde, and dimethylnitrosamine)[27] as well as acetophenone, phenol, α-hydroxyacetophenone, and epoxyethane[26] have been identified by chromato-mass-spectrometry. When analogous experiments were carried out with the preliminary passage of the air analysed through a glass filter treated with a 1% or 10% $Na_2S_2O_3$ solution, the content of the halogenation and oxidation products in the substances collected on the filter was sharply reduced.[26,27]

**Table 1.** The formation of 1,2-dichlorocyclohexane in the concentration of cyclohexenes and chlorine on Tenax.[24]

| Inorganic contaminants* | | | | Cyclohexene* | 1,2-Dichlorocyclohexane** |
|---|---|---|---|---|---|
| $O_3$ | NO | $NO_2$ | $Cl_2$ | | |
| 0 | 0 | 0 | 104 | 90 | 0 |
| 100 | 0 | 0 | 0 | 90 | 0 |
| 0 | 300 | 350 | 104 | 90 | 0 |
| 160 | 0 | 0 | 104 | 818 | 110 |
| 0 | 0 | 0 | 104 | 818 | 100 |
| 180 | 0 | 0 | 104 | 818 | 120 |
| 0 | 0 | 0 | 104 | 818 | 110 |
| 0 | 100 | 0 | 104 | 818 | 100 |
| 100 | 0 | 0 | 0 | 818 | 0 |
| 720 | 0 | 0 | 104 | 818 | 120 |

*The concentrations $10^7c$ (wt.%) are quoted.
**The amount of 1,2-dichlorocyclohexane formed (in ng) is indicated.

When styrene is concentrated by sorption in a tube with activated charcoal, there is a potential risk of a change in the initial concentration of styrene as a result of catalytic reactions.[28] During the thermal desorption of $C_4$–$C_5$ light hydrocarbons concentrated on activated charcoal, some of them isomerise at 150–250 °C, giving rise to compounds previously absent from air—*cis*-but-2-ene and *cis*-pent-2-ene.[7]

The coadsorption of impurities in the trap with the sorbent also alters the composition of the sample. The study of the quantitative characteristics of the sorption of benzene on graphitised carbon black and of their influence on the relative retention volumes of n-pentane, acetone, nitromethane, propanol, and tetrahydrofuran showed that the coadsorption of benzene can lead (depending on the degree of surface coverage of the carbon black by benzene) both to an increase (for a surface coverage of 0.3–0.5) and a decrease (for a surface coverage of less than 0.3) of the retention parameters of the impurities.[16] This is illustrated in Fig.1, which shows that the degree of sorption of acetone by Carbopack C is reduced as the free surface of the adsorbent is occupied by the benzene molecules.

Water vapour is a particularly strong competitor towards the sorption of organic impurities.[15] According to current ideas,[29] the principal cause of the strong adsorption of $H_2O$ molecules on carbonaceous sorbents is the primary adsorption centres, which are present on the surfaces of the walls of the adsorbent pores and are capable of forming hydrogen bonds. The strong sorption of $H_2O$ and $CO_2$ [15] alters the sorption of the other impurities and leads to anomalies in the process involving their concentration.[3] The polar $H_2O$ molecules can displace the previously concentrated organic impurities from the sorbent, can dissolve them, and can alter the dynamics and kinetics of the sorption of subsequent compounds in the trap. When the weight fraction of $H_2O$ in the activated charcoal is at the level of 0.02, the error of the determination is low,[15] but in the presence of an $H_2O$ weight fraction of 0.15 it amounts to 45% for ethanol and increases by 6–12% for butanol and acetone.

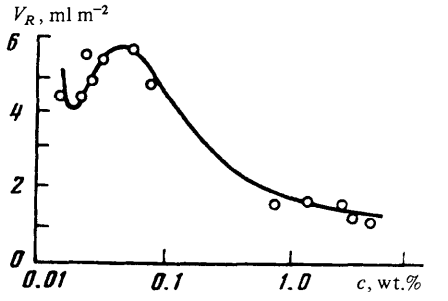



**Figure 1.** Dependence of the retention volume ($V_R$) of acetone on the benzene concentration ($c$) in the vapour phase on Carbopack C at 10 °C.[16]

Sulphates and nitrates can be formed in the preparation of the sample for analysis as a result of the reactions of some of the trapped substances with the sulphur- and nitrogen-containing gaseous oxides and acid vapours ($SO_2$, $NO_2$, $HNO_3$, etc.) present in the matrix. The above artefacts, associated with side reactions on the surfaces of sorbents, can cause an error in the determination of the impurities amounting to 8–11 mg m$^{-3}$.[8]

## 2. The Reaction-Sorption Method for the Concentration of Impurities

The reaction-sorption method (RSM) makes it possible to prevent the chemical interaction of the sample components during the concentration process and to reduce to a minimum the influence of coadsorption.[3,30,31] The essential feature of the RSM involves the preliminary removal of the intefering impurities during the sampling of air with the aid of a reactor containing sorbents or chemical reagents and placed before the concentrator. As a result of this, only the target components enter the trap with the sorbent and the method exhibits a high selectivity, which can vary within wide limits when the reactor packing is altered.[3,30] The fractionation of the compounds in the sample before their concentration not only improves the kinetics and dynamics of the sorption of the target components but also creates conditions for their more reliable identification because most of the sample components (approximately 70–80%) remain in the pre-column-reactor.

Preliminary absorption of compound interfering with analysis had already been used earlier to increase the selectivity of the determination of the toxic impurities in the air of the working zone in industrial undertakings by a linear colour [comparison?] method.[30] The analysis was carried out via a

two-step scheme: chemical separation and detection (Fig.2, Scheme *A*). The colour reactions of the impurities analysed with appropriate reagents (colorimetric and linear colour [comparison?] methods).

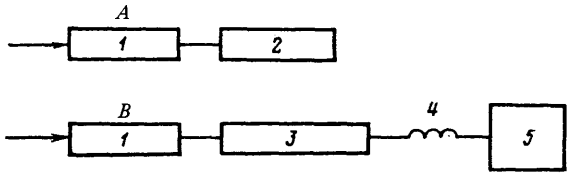



**Figure 2.** RSM schemes for the analysis of impurities: 1) column with sorbents and chemical reagents (pre-column-reactor); 2) column with indicator powder; 3) concentration column with sorbent; 4) chromatographic column; 5) chromatographic detector.

In the chemical-sorption versions of the concentration and gas-chromatographic determination of impurities,[30,31] it is useful to employ the following analytical scheme: chemical (or physical) separation—concentration—chromatographic separation—detection (Fig.2, Scheme *B*). In this version the selectivity of the separation of impurities (the overall selectivity of the separation in the pre-column and in the chromatographic column) is much higher than in the first version (Scheme *A* in Fig.2). The limit of the detection in analysis using Scheme *B* is usually lower by 3–4 orders of magnitude than in the linear colour method for the determination of impurities in air.[30]

On the other hand, the reaction-sorption method for the concentration of impurities differs significantly from the subtraction method employed in gas chromatography[31] and presupposes the selective absorption of the non-target components in combination with the subsequent concentration and chromatographic determination of the target components.[3,30] The reaction-sorption concentration method belongs to a new group of hybrid methods and is free from many of the disadvantages characteristic of the traditional procedures for the trapping of impurities from contaminated air.

We shall consider the possibilities of the RSM in its application to the solution of certain practical problems in the analysis of contaminated air.

## 3. Increase in the Reliability of the Determination (Decrease of the Probability of the Chemical Interaction of the Sample Components)

The extensive possibilities for the variation of the composition of the sorbents and chemical reagents in the packing within the fore-column-reactor make it possible to use RSM in solving a number of problems in the determination of small amounts of reactive chemical impurities in air (Table 2).

*(a) Determination of corrosive gases.* Apart from their interaction with the packing of the chromatographic column and their absorption by the connecting tubes in the chromatograph, reactive gases frequently react with one another (particularly when they are concentrated on sorbents), which hinders their gas-chromatographic determination or makes it impossible.[21] An example may be provided by the reactions in the $Cl_2$–HCl–$ClO_2$–$O_2$–$NO_2$ system, characterising the contamination of air in undertakings where inorganic syntheses are carried out.[38]

**Table 2.** Certain versions of the determination of impurities in air by the RSM method.

| Compounds analysed | Sorbent in precolumn | Impurities absorbed | Target components | Refs. |
|---|---|---|---|---|
| $SF_6$, $SF_4$, $SF_2$, HF, $S_2F_2$, $SOF_2$, $COF_2$, $SO_2F_2$ | NaF | $F_2$, HF | $SF_4$ | [32] |
| $Cl_2$, $ClO_2$, HCl, $O_2$, $NO_2$ | glass fibre, −78° C | $ClO_2$ | $Cl_2$, $NO_2$ | [21] |
| $N_2O$, NO, $NO_2$, $N_2O_4$ | 13X molecular sieve | $N_2O$, $NO_2$, $N_2O_4$ | NO | [33, 34] |
| CO, $CO_2$, $CH_4$, light hydrocarbons | 13X zeolite, Ascarite, activated charcoal, 0 °C | $CO_2$, $CH_4$, light hydrocarbons | CO | [35] |
| Olefins, $NO_2$, paraffins, $Cl_2$ | $Na_2S_2O_3$ | $NO_2$, $Cl_2$ | hydrocarbons | [36] |
| Organic and inorganic acids, aldehydes, ketones | $Na_2CO_3$ | acids | ketones, aldehydes | [36] |

When the concentration process is carried out on solid sorbents (silica gas, graphitised carbon black, porous Teflon, etc.), the components of this mixture interact even at ordinary temperatures with formation of more toxic but less reactive substances.[37,38] In many cases the principal (overall) reaction is that of chlorine and nitrogen oxides:

$$ClO_2+3NO_2 \rightarrow NO_2Cl+N_2O_5. \qquad (1)$$

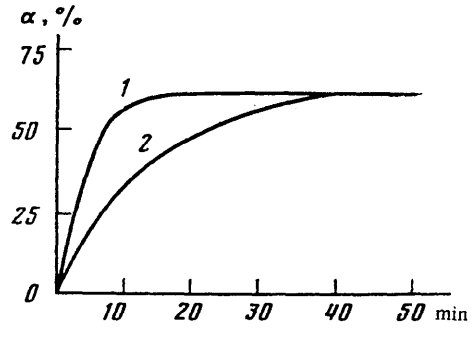



**Figure 3.** Dependence of the degree of conversion of $NO_2$ on the initial $NO_2$ : $ClO_2$ ratio; $NO_2$ : $ClO_2$ ratio: 1) 3 : 1; 2) 1 : 1.[38]

Some idea about the process kinetics can be provided by the plot of the dependence of the degree of conversion of $NO_2$ on the initial concentrations of the oxides (Fig.3). When air is passed through a tube with the sorbent (for example, graphitised carbon black) at 20–35 °C, the degree of reaction of $ClO_2$ with $NO_2$ is not less than 50% (Fig.3). If account is taken also of the numerous side reactions[38] and

of the decomposition of the concentrated sample in the thermal desorption process at 150 °C,[37,38] i.e.

$$2NO_2Cl \rightarrow 2NO_2 + Cl_2 + O_2 \qquad (2)$$

then it becomes evident that a mixture of corrosive gases having a composition different from that in the initial air enters the chromatographic column (Fig.4); as a result of the different reactions in the sample, the amount of $NO_2$ and $ClO_2$ diminishes and that of $Cl_2$ increases. A pre-column containing glass wool and cooled with dry ice traps the $ClO_2$ impurity from the mixture analysed before chromatography. After this, the gas-chromatographic determination becomes significantly more accurate—the standard deviations for $Cl_2$, $NO_2$, and $ClO_2$ decrease by a factor of 2–3.[38]

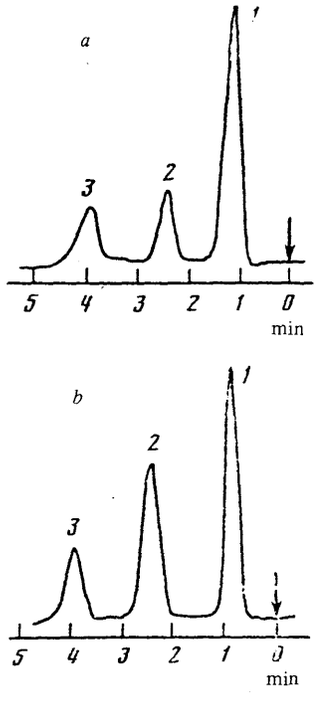



**Figure 4.** Chromatographic separation of the $Cl_2$, $ClO_2$, and $NO_2$ impurities:[38] *a*) in the usual method; *b*) in the method using a pre-column; 1) $Cl_2$; 2) $NO_2$; 3) $ClO_2$.

*(b) Nitrogen oxides.* The direct determination of NO, $NO_2$, $N_2O_4$, and $N_2O$ is difficult as a consequence of the higher reactivity of these gases.[21] The method of reaction gas chromatography (RGC), which consists in the conversion of nitrogen oxides into organic derivatives[34] requires the preliminary oxidation of NO to $NO_2$ [39] with subsequent estimation of the NO content from the difference between two determinations ($NO_2$ and the sum of NO and $NO_2$). The individual determination of NO in a mixture of nitrogen oxides† which have similar properties (and are therefore difficult to distinguish) is feasible when the mixtures are concentrated by the RSM.[33,40]

The determination of NO by the RGC method in conjunction with the RSM consists in passing the air to be analysed through a pre-column (16 cm × 5 mm) containing the 13X molecular sieve (0.5–0.25 mm fraction) subjected to a preliminary heat treatment in the course of 4 h in a stream of dry nitrogen at 350 °C. This pre-chromatographic reactor absorbs 95–97% of the admixture of $N_2O$, $NO_2$, and $N_2O_4$, but does allow NO to go through; the loss of NO (after the preliminary conditioning of the fore-column with a mixture of nitrogen oxides, in which the concentration of NO is 10 mg $m^{-3}$, for 30 min) is not more than 0.5–1.2 wt.%.

When this analytical scheme is employed, the NO content in the mixture of nitrogen oxides is determined not from the difference between the two measurements but directly (after the necessary procedure involving the oxidation of NO to $NO_2$ by $H_2O_2$) in the form of a derivative (nitrobenzene) obtained by the reaction of $NO_2$ with benzene in the presence of concentrated sulphuric acid.[39] The limit of detection of nitrogen oxides by this method is ~$10^{-6}$ wt.% with a relative standard deviation of 0.30. Fig.5 illustrates the chromatogram for the determination of NO (in the form of $NO_2$) in the exhaust gases from diesel engines, obtained using the above procedure and the RSM.[33,40]

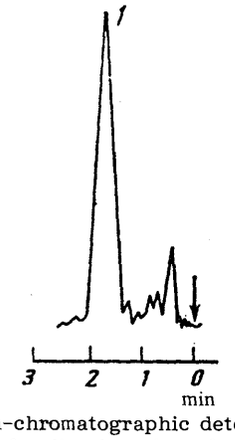



**Figure 5.** Reaction-chromatographic determination of $NO_2$ in the exhaust gases of a diesel engine after the conversion of $NO_2$ into nitrobenzene[33] (glass 1.5 m × 4 mm column with 15% of Apiezon L on Chromaton N; electron capture detector; column temperature 120 °C; detector temperature 275 °C): 1) nitrobenzene; $NO_2$ concentration in air 8 mg $m^{-3}$.

*(c) Sulphur fluorides.* Analysis of a complex mixture of corrosive sulphur fluorides ($SF_6$, $SF_4$, $S_2F_2$, $SO_2F_2$, $SOF_2$, HF, and $F_2$) is made very difficult by the active interaction of the extremely reactive HF and $F_2$ with all sorbents and constructional materials of chromatographs.[21,40] This interaction results in a low reproducibility of the determination of the target component—sulphur tetrafluoride, whose toxicity is higher than that of phosgene.[32] The content of the $SF_4$ to be determined depends on the volume of the sample injected, the presence of moisture, the ratio of the components in the mixture of fluorides, and the amount of HF and $F_2$. The relative standard deviation then varies within wide limits and can be between 0.40 and 0.8.

† The separate determination of NO and $NO_2$ is of fundamental importance for industrial labour hygiene.

Concentration of the fluoride impurities by the RSM made it possible to eliminate the influence of the reactive $F_2$ and HF. The air analysed is first passed through a pre-column (4 cm × 4 mm) with sodium fluoride (0.5–0.25 mm fraction) and the fluoride impurities are then concentrated in a trap with Porapak Q.[40] The pre-column retains almost 100% of the admixture of the corrosive $F_2$ and HF, but does not absorb $SF_4$ at low concentrations (0.1–1.0 mg $m^{-3}$). The degree of absorption of sulphur tetrafluoride by the pre-column is less than 0.4%.[32] The chromatogram of the mixture of sulphur fluorides formed in the air of a foundry during smelting in a sulphur hexafluoride atmosphere is presented in Fig.6. Concentration of the fluoride impurities by the RSM makes it possible to determine small amounts of $SF_4$ (the limit of detection is 0.05 μg) with a relative stnadard deviation of 0.22.[32,40]

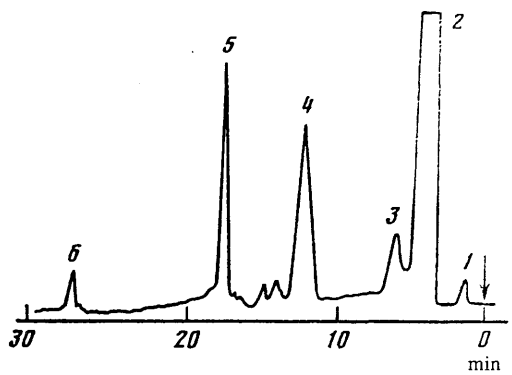



**Figure 6.** Chromatogram of sulphur hexafluoride and admixtures of lower sulphur fluorides on a 3 m × 4 mm stainless steel column with Porapak Q at 50 °C after the RSM removal of $F_2$ and HF from the mixture:[32] 1) carbon tetrafluoride; 2) sulphur hexafluoride; 3) sulphur monofluoride; 4) sulphur tetrafluoride; 5) sulphuryl fluoride; 6) thionyl fluoride.

*(d) Hydrocarbons.* It is much more difficult to discover the cause of the change in the composition of the impurities in air to be analysed in the determination of organic compounds (chemical interaction with the sorbent, coadsorption, polymerisation reactions, etc.) than in the determination of reactive inorganic gases, where chemical interaction usually predominates.[3,40] In the study of the processes involving the sorption (concentration) of organic impurities on solid sorbents with a high surface area, such changes are most clearly manifested in the thermal desorption of the sample from the sorbent, whereupon the concentrated impurities undergo thermal degradation and isomerisation reactions.[3,7,31] This factor becomes evident when the RSM concentration of the $C_5$–$C_7$ alkanes, isopentane, and hex-1-ene impurities in a trap with activated BAU charcoal is considered (Table 3).

Table 3 shows that the RSM concentration procedure makes it possible to obtain much more accurate isopentane contents than under the conditions of the traditional concentration of the hydrocarbon impurities on charcoal with subsequent thermal desorption. This finding can be accounted for by the isomerisation of the n-pentane, isopentane, and hex-1-ene impurities at the thermal desorption temperature (200 °C), which results in the formation of *cis*-but-2-ene and *cis*-pent-2-ene.[7]

**Table 3.** The reaction-sorption concentration* of isopentane in the presence of low-boiling hydrocarbons**.[36]

| $c_0$ | GC | | GC-RSM | |
|---|---|---|---|---|
| | $S$ | $c \pm \delta$ | $S$ | $c \pm \delta$ |
| 52 | 26 | 70±27 | 12 | 55±13 |
| 64 | 34 | 82±36 | 15 | 70±16 |
| 80 | 38 | 93±40 | 20 | 75±21 |
| 91 | 40 | 110±42 | 22 | 88±23 |
| 102 | 56 | 120±59 | 25 | 104±26 |

Notation: $n$ is the number of replicate determinations ($n = 6$), $c_0$ the initial isopentane concentration (mg $m^{-3}$), $c$ the arithmetical mean isopentane concentration for $n$ replicate determinations found in the presence of admixtures of other hydrocarbons (mg $m^{-3}$), $S$ the standard deviation (mg $m^{-3}$), $c \pm \delta$ the confidence interval of the concentration $c$ (mg $m^{-3}$), $\delta$ the accuracy of the direct measurement of $c$ (for a small number of measurements, $\delta = tS/n^{2/3}$, where $t$ is the Student statistic).

*The pre-column with 5A molecular sieve absorbs hydrocarbons having the normal structure.

**The values of $S$ and $c \pm \delta$ (fiducial probability $P = 95\%$), obtained by the traditional gas-chromatographic method (GC) and the method involving the RSM concentration procedure (GC–RSM) are quoted).

## 4. Reduction of the Influence of the Coadsorption of Impurities

The composition of the sample of organic impurities to be concentrated is usually distorted by the coadsorption of impurities in the trap-concentrator with the sorbent.[3,7,41] This process, which influences the validity of the analysis, takes place invariably when components of any mixtures of harmful substances are extracted from air.[3]

In order to explain the nature and mechanism of coadsorption and its influence on the parameters of the impurity sorption (concentration) process on sorbents, it is necessary to examine the behaviour of impurities in the sorption–desorption system.

*(a) Sorption dynamics.* In the concentrator containing the sorbent, the impurities to be analysed undergo frontal enrichment. Their concentration in the gas then usually diminishes sharply as air passes through the layer of sorbent. The end of the operation of the reactor (its becoming "spent") is assumed to be the instant of the appearance of the test substance (substances) beyond the layer of sorbent—to so-called "breakthrough".# Impurities are distributed in the sorbent layer in accordance with their adsorption isotherms.[42]

# In analytical practice "breakthrough" is defined as the appearance of the impurities to be analysed beyond the sorbent layer, their concentration amounting to 5 or 10% of the initial concentration of the harmful substances in air.[5,41]

The maximum operating time of the trap with the sorbent (the time before breakthrough) $\tau$ can be determined from the Shilov equation[42,43]

$$\tau = KL - \tau_0, \quad (3)$$

where $K$ is the coefficient of the protective action of the layer, $L$ the length of the sorbent layer, and $\tau_0$ the time to the end of protective action by the layer. The coefficient of protective action by the layer is defined by the expression

$$K = a_0/\omega c_0, \quad (4)$$

where $a_0$ is the equilibrium static activity, $\omega$ the flow rate, and $c_0$ the initial concentration of impurities in air.

The Shilov equation can be also presented in the following form (the Mecklenburg equation):

$$\tau = K(L - h). \quad (5)$$

It is assumed that only the adsorbent layer with the length $L-h$ is fully saturated while the layer whose length is $h$ remains unsaturated. The graphical representation of this layer is illustrated in Fig.7. The length of the unsaturated or unused layer $h$ is determined from the intercept on the abscissa axis obtained when the straight line $B$ (dashed line) is produced.[43]

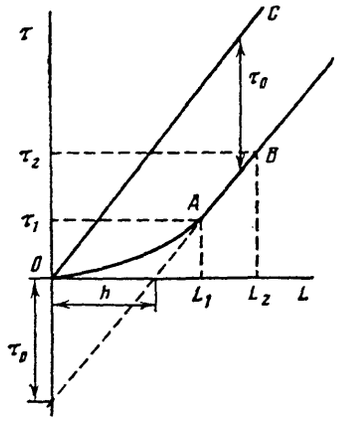



**Figure 7.** Dependence of the sorption time $\tau$ on the length of the sorbent bed $L$:[43] OC straight line—theoretical dependence of the sorption time on the length of the absorber bed for an infinitely high rate of sorption; OAB curve—actual dependence of the sorption time on the length of the absorber bed.

On comparing the Shilov and Mecklenburg equations (3) and (5), it is possible to find the relation between the loss of the time of protective action $\tau_0$ and the length of the unused sorbent layer $h$:

$$\tau_0 = Kh. \quad (6)$$

During the RSM concentration process in the pre-column, all (or most of) the accompanying impurities are removed (adsorbed), which entails a change in the sorption dynamics of the target sample components on the sorbent in the trap. It follows from Eqn.(6) that Fig.7 that a decrease of $h$ leads to a decrease of $\tau_0$. The concentrator with the sorbent located beyond the pre-column therefore works more effectively and its sorption capacity with respect to the target components increases.

*(b) Coadsorption dynamics.* The impurity adsorption processes in the trap with the sorbent and the influence of the sorption of the accompanying impurities on the adsorption of the target components can be represented by several equations analogous to the equation of the Langmuir adsorption isotherm.[3,42]

In the case of the simultaneous adsorption of the target component (whose concentration in air is designated by $c_1$) and of the accompanying impurities (concentrations $c_i$), the adsorption of the target component can be represented by the following equation:[36]

$$a_1 = b_1 c_1 N \Big/ \left[1 + \sum_{i=1}^{m} \frac{b_i c_i}{K_i}\right], \quad (7)$$

where $m$ is the number of impurities, $N$ the maximum possible number of active centres per unit area of the adsorbent, $K_i$ the specific degree of saturation of the active centre of the sorbent by the test substance, and $b_1$ the adsorption coefficient. Eqn.(7) can also be written in the following way:

$$a_1 = b_1 c_1 N \Big/ \left[1 + \frac{b_1 c_1}{K_1} + \sum_{i=2}^{m} \frac{b_i c_i}{K_i}\right]. \quad (8)$$

In this equation the term $\sum_{i=2}^{m} b_i c_i / K_i$, which determines the coadsorption of admixtures, significantly reduces the degree of adsorption of the main substance, impairing the degree of its concentration and interfering with the formation of a representative sample. This leads to systematic errors in the determination of microamounts of harmful substances in air, which it is virtually impossible to obviate in the usual version of analysis.[3,36] The employment of a pre-column enables one to increase appreciably the efficiency of the concentration of the target impurity, whose relative concentration increases in the course of the RSM concentration process to a significantly greater extent than in the usual version of the concentration procedure on sorbents. This factor creates preconditions for increasing the degree of enrichment of the sample, for reducing the detection limit for the target components (other analytical conditions being equal), and for the preparation of a representative sample of the impurities in air.[3,36,49]

*(c) Decrease of the degree of coadsorption.* The influence of coadsorption can be so great that the losses of the target component during the concentration of impurities can amount to 20–50%, which is 7–8 times greater than the losses due to the incomplete desorption of the impurities from the sorbent in the extraction of individual compounds from air.[3] The usual version of the concentration from air of small amounts of vinyl chloride in the presence of admixtures of chlorine-containing hydrocarbons which accompany it under real conditions (overall concentration 110 mg $m^{-3}$) may serve as an example. At a vinyl chloride concentration of 10 mg $m^{-3}$, a temperature of 20 °C, and for an air flow rate of 0.4 litre $min^{-1}$, breakthrough occurs after 40 min, while in the presence of impurities the time before breakthrough is reduced to 24 min. The losses of vinyl chloride in the concentration process change correspondingly from 6.2% in the concentration of vinyl chloride alone to 44% when vinyl chloride is concentrated in the presence of admixtures of chlorine-containing hydrocarbons.[49]

The coadsorption of admixtures of other organic compounds, which frequently accompany vinyl chloride in air from the workplace involved in the processing of polymers based on poly(vinyl chloride),[3,50,51] can reduce to an even greater extent the degree of adsorption of the monomer impurity by the adsorbent than halogen-containing compounds (Fig.8).

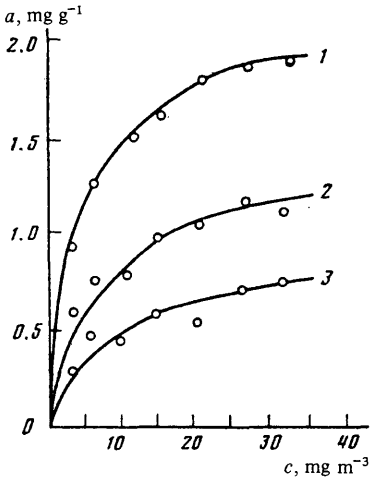



**Figure 8.** The influence of the coadsorption of accompanying admixtures (propene, methanol, acetone, acetaldehyde, and tetrachloroethylene) on the efficiency of the sorption of vinyl chloride by activated charcoal:[50] impurities: 1) vinyl chloride (adsorption isotherm); 2) vinyl chloride + admixtures (1 : 1); 3) vinyl chloride + admixtures (1 : 8); $a$ = amount of vinyl chloride adsorbed by the charcoal; $c$ = concentration of impurities.

The use of a pre-column in all the cases enumerated above gives rise to a positive result, increasing the time (volume) before the breakthrough of the target components of the sample, increasing the sorption capacity of the concentrator with the sorbent, and tending to reduce the limit of detection of the impurities. This can be illustrated by experimental data for the sorption and RSM concentration of organic impurities of different nature in a trap containing an activated charcoal (Tables 4–6).

A consequence of the increase in the volume before the breakthrough of the test substances was the corresponding increase (by a factor of 2–3) of the sorption capacity of the sorbent with respect to the target components (Table 5). The effectiveness of the sorption in the concentrator with BAU charcoal–pre-column system was compared with the analogous data calculated from the results of sorption experiments for individual compounds on the above adsorbent using literature data.[3,5,7,13,44–48] The sorption capacity was calculated from the results of the chromatography of the test mixtures, taking into account the instant of breakthrough, or was determined by a direct method involving the weighing of the tube containing the charcoal before passing the air sample through it and after breakthrough.

Tables 4 and 5 show that the removal of the accompanying admixtures by the pre-column (the sorption characteristics were calculated for each compound quoted in the Table on the assumption that all the remaining compounds are accompanying admixtures) makes it possible to avoid coadsorption and to increase the efficiency with which the target components are trapped.

**Table 4.** The change in quantity before breakthrough* using the RSM concentration of impurities on activated charcoal.[3,36]

| Compound | $c$, mg m$^{-3}$ | PDK***, mg m$^{-3}$ | $V_{br}$, litre/100 mg of charcoal | | |
|---|---|---|---|---|---|
| | | | without pre-column | with pre-column | from data in Refs. 44–48** |
| Benzene | 100 | 5 | 30 | 53 | 42 |
| Toluene | 50 | 50 | 12 | 20 | 23.1 |
| Hexane | 100 | 100 | 14 | 35 | 33 |
| Ethyl methyl ketone | 100 | 200 | 3 | 8.8 | 8.2 |
| Ethanol | 1000 | 1000 | 4.5 | 11 | 3–25 |
| Tetrachloroethylene | 100 | 10 | 8 | 24 | 33.2 |
| Triethylamine | 100 | 10 | 4 | 8 | 6.6 |
| Dipropyl sulphide | 100 | 50 | 12 | 20 | 22 |

*The volume before breakthrough $V_{br}$ was determined for individual substances in the presence of the accompanying admixtures.

**The values of $V_{br}$ used in the table were selected from the published literature data[44–48] subject to the requirement that the experimental conditions under which all the tabulated data were obtained are similar.[36]

***Transliterated Russian abbreviation which the authors do not define. Its significance is obscure (Ed.of Translation).

**Table 5.** The sorption capacity of the concentration tube containing BAU activated charcoal in the trapping of organic vapours from air.[36,49,51]

| Compound | Sorption capacity, mg/g of sorbent | | |
|---|---|---|---|
| | without pre-column | with pre-column | according to data in Refs. 7, 13, and 45–48 |
| Benzene | 30 | 53 | 60 |
| Toluene | 80 | 210 | 280 |
| Hexane | 18 | 35 | 42 |
| Ethyl methyl ketone | 36 | 75 | 90 |
| Ethanol | 15 | 35 | 42 |
| Tetrachloroethylene | 26 | 78 | 100 |
| Triethylamine | 20 | 38 | 35.5 |
| Dipropyl sulphide | 64 | 170 | 156 |

The somewhat greater sorbent capacity given in the literature can be accounted for by the fact that the values quoted in the literature were calculated for pure individual substances, while a pre-column does not remove entirely the accompanying admixtures. This influences the residual sorption (coadsorption), inducing some decrease in the degree of sorption of the target components (approximately by 15–25%).

The increase in the sensitivity of the determination is a consequence of the more effective sorption of admixtures of the target components in the RSM concentration process. Table 6 shows that the reaction-sorption concentration process makes it possible to reduce the limit of detection of principal classes of organic impurities by a factor of ~2–3.

An important result of the use of the RSM, associated with the elimination of the coadsorption of admixtures, is the improvement of virtually all the metrological characteristics of the method. This can be illustrated by the data in Table 7

which presents the results of the determination of small amounts of the vinyl chloride impurity. Comparison of the results the determination of this gas by two different methods (gas chromatography and gas chromatography + RSM) shows that the latter should be preferred (Table 7).

**Table 6.** The sensitivity of the determination ($\alpha$) of toxic impurities.[3,36,49,51]

| Compound | Sensitivity of determination*, mg m$^{-3}$ | |
|---|---|---|
| | $\alpha_1$ | $\alpha_2$ |
| Aromatic hydrocarbons | 0.10 | 0.03 |
| Paraffinic hydrocarbons | 0.10 | 0.06 |
| Halogenohydrocarbons | 0.50 | 0.25 |
| Oxygen-containing organic substances | 0.80 | 0.40 |
| Organosulphur compounds | 0.60 | 0.40 |
| Aromatic amines | 0.20 | 0.10 |

*$\alpha_1$ and $\alpha_2$ are the average detection limits in the usual version of the chromatographic analysis with the aid of a flame-ionisation detector and in the RSM analysis respectively.

**Table 7.** The validity of the analytical results in the determination of vinyl chloride*.[52]

| GC | | | GC-RSM | | |
|---|---|---|---|---|---|
| $s$ | $s_r$ | $c\pm\delta$ | $s$ | $s_r$ | $c\pm\delta$ |
| 0.28 | 0.40 | 0.70±0.20 | 0.17 | 0.18 | 0.98±0.12 |
| 0.16 | 0.36 | 0.44±0.12 | 0.56 | 0.14 | 0.56±0.10 |
| 0.05 | 0.45 | 0.11±0.04 | 0.03 | 0.30 | 0.10±0.02 |

Notation: $m$ is the sample size (μl) and $S_r$ the relative standard deviation; for the significance of the remaining symbols, see Table 3.
*The test was carried out by comparing the results obtained using the RSM with those obtained in the usual version of gas chromatography (for $n = 10$ and $P = 95\%$; $m = 10$ μl).

### 5. Improvement of the Chromatographic Separation

An important aspect of the use of the RSM in the improvement of the chromatographic separation of impurities. The absorption in the pre-column of the accompanying admixtures increases the efficiency of the separation of the target components from other compounds in the sample. Apart from the possibility of securing more reliable information about the composition of the compounds to be analysed, this procedure increases the accuracy of the determination of the target components.[3,34,36]

The direct (without the preliminary concentration of the impurities) gas-chromatographic determination of small amounts of CO, one of the principal contaminants in the air from the workplace, may serve as an example.[35] The absorption of the $C_1$–$C_3$ light hydrocarbons, $O_2$, $N_2$, $CO_2$, and water vapour, which interfere with the determination of CO, in a pre-column with Ascarite, 13X molecular sieve, and activated charcoal at 0 °C makes it possible to achieve a satisfactory separation of CO from $CH_4$ and other admixtures on an analytical column with 5A zeolite and to increase the accuracy of the determination of the concentration of CO. For CO concentrations in the range 20–50 mg m$^{-3}$, the use of the RSM permits the reduction of the error of the determination from 18–20% to 12%. A fore-column containing a layer of Chromosorb W impregnated with a 0.1 M solution of $SnCl_2$ (for the absorption of $H_2S$) and a layer of activated charcoal (210 mg) for the adsorption of oxidisable hydrocarbons is suitable for an analogous purpose.[53] In order to fractionate the mixture of reactive gases in the determination of $SO_2$ in air, the nitrogen oxides, which interfere with the determination, are absorbed in an absorber containing a 0.6% solution of sulphamic acid, while $H_2S$ is removed in a pre-column with an aqueous solution of $Pb(CH_3COO)_2$.[54]

Different versions of the RSM concentration process have been used to improve the chromatographic separation of impurities comprising hydrocarbons,[49] halogenohydrocarbons, and oxygen-containing organic compounds,[36] as well as reactive inorganic gases[34] and various inorganic compounds.[40] In order to reduce the error in the determination of low concentrations of a hydrazine and asymmetric dimethylhydrazine aerosol, the admixtures of ethyl acetate, 2-furoaldehyde, and their derivatives, which interfere with the analysis, were first removed from the mixture (in the course of the extraction of the above impurities from air) by passing the mixture through a pre-column.[55]

### 6. The Removal of Moisture

One of the important conditions for the prevention of loss in mixtures of air contaminants to be analysed, associated with coadsorption, is the removal of moisture in the course of the extraction of the impurities from air.[3,21,34] This problem has several different solutions,[34,40] the best of which involves the application of reaction-sorption systems.[30,31] The use of the RSM concentration process, which provides for the removal of $H_2O$ in pre-columns with zeolites, does not affect other compounds in the sample and does not distort the composition of the latter.[3]

In the automatic determination of ultramicroconcentrations of CO in the troposphere with the aid of an He-ionisation detector, an additional short column with the 5A zeolite, which is periodically regenerated, is placed before the analytical column in order to separate the interfering impurities ($H_2$, $O_2$, $N_2$, $CO_2$, and $H_2O$) from the bulk.[56] Another version of the RSM is based on the employment of a short column (7 cm × 4 mm) with 3A zeolite activated for several hours in a stream of dry nitrogen at 300 °C.[57] With the exception of $CH_3OH$, this pre-column vigorously retains $H_2O$, but does not sorb organic impurities. The 3A molecular sieve can therefore be regarded as the ideal drying agent for the determination of toxic microimpurities in air.[3,34,57]

## IV. IDENTIFICATION OF IMPURITIES IN THE REACTION-SORPTION CONCENTRATION METHOD

The main problem in the analytical chemistry of air contaminants is that of the reliable identification of harmful impurities in complex mixtures of air contaminants.[3,30] The traditional scheme for the gas-chromatographic analysis of contaminated air presupposes the absorption of all the chemical compounds present in air on solid sorbents, the extraction of the concentrated impurity by a solvent, and the gas-chromatographic separation and identification of the sample components.[2,3] All compounds, without exception, extracted from air are detected on the chromatogram. This

factor hinders greatly the identification of impurities, since in the general case one has to deal with mixtures of impurities belonging to different classes.[4,5-7]

The difficulty of securing reliable information about the composition of complex mixtures in harmful organic substances§ is due to the insignificant differences between the retention characteristics of the impurities (for example, the Kovac indices).[3,30] The use of a kind of "chemical filter" (such as the RSM) presupposes the successive removal from the mixture to be analysed of specific classes of organic compounds, which significantly facilitates the chromatographic identification of the contaminants and makes it more reliable.[3]

## 1. Determination of Hydrocarbons

The simplest analytical problems which can be solved with the aid of the RSM concentration procedure is the determination of toxic hydrocarbon impurities in any complex mixtures of air contaminants.[31] This is because hydrocarbons are the most inert organic compounds and the accompanying admixtures of substances with different functional groups can be removed from the air to be analysed by means of a pre-column with a powerful reducing agent such as lithium tetrahydroaluminate without affecting the hydrocarbons themselves.[3,31,58]

A pre-column containing phosphoric acid, Versamid 900, lithium tetrahydroaluminate, and lead acetate is effective for this purpose.[59] Such a reactor absorbs satisfactorily all organic impurities with the exception of hydrcarbons. This method has been used successfully for the identification and quantitative gas-chromatographic determination of hydrocarbon impurities in the atmosphere in the workplace in factories (the gas is evolved from raw and pure rubbers, polymeric materials, solvent vapours, thermal degradation products, etc.).[3,30]

A pre-column with Chromosorb P impregnated with a solution of chromium trioxide in concentrated sulphuric acid has been used for the selective absorption of reactive organic impurities from air in a study of atmospheric photochemical reactions.[60] At a temperature of 72–77 °C, the reactive unsaturated hydrocarbons, involved in the formation of the photochemical "smog" which has a fatal effect on many plant species, are extracted from the air, analysed with the aid of such a reactor, and reliably identified.[30]

For the gas-chromatographic identification of the highly toxic styrene, air has been blown[61] through a glass pre-column (6–16 cm × 4 mm), which allows only the compound sought to pass a trap containing Tenax GC. Esters were then absorbed in a fore-column with 10% NaOH on Shimalite, while carbonyl-containing compounds were absorbed in a reactor containing a 2% solution of 2,4-dinitrophenylhydrazine deposited on glass beads. Styrene passed through these pre-columns unchanged and, after being concentrated on a porous polymeric sorbent, its content was determined on a chromatograph with a flame-ionisation detector.

A novel method for the preliminary separation of a complex mixture of the products of the oxidation of various motor fuels has been proposed.[62] Nucleophilic compounds (aldehydes, ketones, alcohols, ethers, esters, etc.) can be selectively absorbed with the aid of a pre-column containing a europium complex of *p*-di(4,4,5,5,6,6,6-heptafluoro-1,3-dioxohexyl)benzene and it is thus possible to separate such substances reliably from alkanes, alkenes, aromatic hydrocarbons, and chlorohydrocarbons before the chromatographic separation of the sample components. The chromatograms of these mixtures after separation on a capillary column 30 m long and containing silicone *SE*-54 are presented in Fig.9. Involatile derivatives of the nucleophiles of the type of bis-(β-diketonates) are then formed in the pre-column by reacting with the polymeric lanthanide complex. So far the number of such examples is small but coordination compounds provide extensive possibilities of effective procedures in the analyses of air contaminants by the separation and preliminary concentration of toxic impurities having various chemical natures.[63]

A set of pre-column-reactors, some of which are listed in Table 8, makes possible reliable group and individual gas-chromatographic determinations of hydrocarbons in complex mixtures of air contaminants having purely hydrocarbon compositions as well as mixtures of hydrocarbons with organic and inorganic compounds having functional groups. After the separation from the hydrocarbon of admixtures which interfere with their identification, the use of the usual procedures in the qualitative chromatographic analysis (for example, the employment of retention indices) enables one to achieve a very high reliability of the results, comparable to that of the results of the chromato-mass-spectroscopic analysis.[3,30,31,68]

**Table 8.** Determination of hydrocarbon impurities with the aid of the RSM analysis.[30,31,64-67]

| Target components | Sorbent in pre-column | Sorbed impurities |
|---|---|---|
| Aromatic hydrocarbons | 5A molecular sieve | n-paraffins, n-olefins, and n-acetylenes |
| Paraffinic, naphthenic, and olefinic hydrocarbons | poly(vinyl chloride) | aromatic hydrocarbons |
| Paraffinic, naphthenic, olefinic, and aromatic hydrocarbons | maleic anhydride* | dienes |
| Paraffinic, naphthenic, and aromatic hydrocarbons | 1 : 1 mixture of $Hg(ClO_4)_2$ and $HClO_4$* or mixture of 20% $HgSO_4$ and 20% $H_2SO_4$* | alkenes and alkynes |
| n-Paraffins and cycloparaffins | conc. $H_2SO_4$* or mixture of 4% $AgNO_3$ and 95% $H_2SO_4$ | aromatic hydrocarbons, olefins, and acetylenes |
| Total hydrocarbons | 10X molecular sieve | aromatic hydrocarbons |

*On a diatomaceous carrier.

## 2. Determination of Oxygen-Containing Organic Compounds

A reactor with silver nitrate, phosphoric acid, Versamid 900, and lead acetate,[69] designed for the isolation of oxygen-containing organic compounds from a mixture of air contaminants, is not quite as reliable as a pre-column for the isolation of hydrocarbons. Together with oxygen compounds, n-paraffinic and naphthenic hydrocarbons pass through the reactor. In order to eliminate their interfering effect, the subsequent gas-chromatographic analysis of the substances concentrated in the trap is carried out on a superpolar stationary liquid phase (SLP) of the type of 1,2,3-tris(cyanoethoxy)propane, which makes it possible to separate the

§ In general there are greater differences between the properties of inorganic compounds and selective detectors, for example, are sufficient for their identification.[3]

paraffin–naphthene fraction from polar derivatives of hydrocarbons. On a column with 15 and 30% of such SLP, methanol emerges after n-decane and tridecane respectively.

This subtraction-isolation method, in which the oxygen-containing substances are separated from non-polar hydrocarbons in the first stage and the substances isolated are subjected to gas-chromatographic analysis in the second stage, is distinguished by a high selectivity, which is made up of the selectivities of the pre-column and the analytical column. This procedure has been used for the identification and reliable determination of toxic admixtures of methanol and other alcohols in the evaporation products of a petrol–methanol fuel,[70] in the determination of volatile compounds in air arising from various solvents,[30,31] and in the analysis of complex mixtures of organic compounds contaminating air in the processing of polymeric materials.[3,36,68]

In the determination of methanol in the exhaust gases from automobile engines,[3,36] where the air in the driving compartment contains aldehydes in addition to methanol, a reactor with $NaHSO_3$ on Chromaton N was used for the reliable identification of methanol with the aid of the RSM.[36] Whilst retaining low-molecular-weight aldehydes, such a pre-column lets methanol and hydrocarbons pass through to the trap with the sorbent; these substances were subsequently separated on a column with 0.2% PEG 1500 on graphitised carbon black and were unambiguously identified using the retention characteristics of the impurities.[3] The action of the pre-column is basedon the interaction of aldehydes with sodium bisulphite involving the formation of a substituted sodium sulphonate in accordance with the equation

$$RCHO+NaHSO_3 \rightarrow RCHOHSO_3Na.$$

In simpler cases, where the air analysed does not contain all possible contaminants but only compounds of specific classes (for example, only hydrocarbons, only halogenohydrocarbons, only alcohols and aldehydes, etc.), the identification of the impurities is greatly simplified (Table 9).

**Table 9.** The RSM concentration and identification of oxygen-containing organic impurities.[2,30,64–67]

| Target components | Sorbent in pre-column | Sorbed impurities |
|---|---|---|
| Oxygen-containing compounds | $AgNO_3$, $H_3PO_4$, Versamid 900, and $Pb(CH_3COO)_2$ | all organic substances other than paraffins and naphthenes |
| Oxygen-containing compounds | Versamid 900 and $AgNO_3$ | halogenohydrocarbons |
| Oxygen-containing compounds | poly(vinyl chloride), $AgNO_3$, Versamid 900 | halogenohydrocarbons, alkylbenzenes, olefins, and acetylenes |
| Aldehydes and ketones | $H_3BO_3$ | primary and secondary alcohols |
| Alcohols | 2,4-dinitrophenylydrazine | aldehydes and ketones |
| Ketones | *o*-dianisidine and 5A zeolite | aldehydes |
| Ethers and esters | 5A molecular sieve | carboxylic acids |
| Lower carboxylic acids | benzidine | aldehydes and ketones |
| Aldehydes, ketones, ethers, and esters | KOH | carboxylic acids |

The RSM concentration procedure has been used successfully also in the solution of certain simpler problems in the chemistry of air contaminants, for example, for the selective

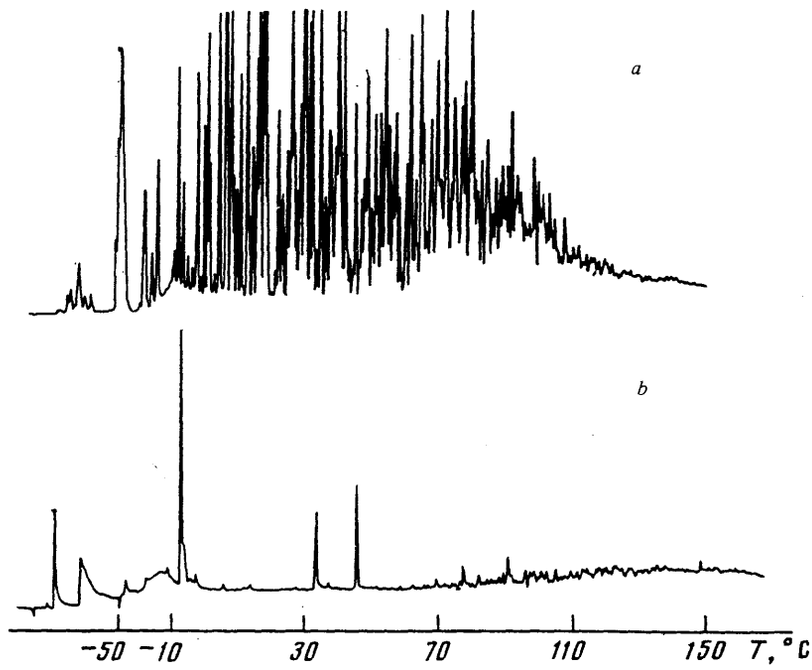



**Figure 9.** Chromatograms of compounds not retained (*a*) and retained (*b*) by the pre-column obtained in the analysis of the vapour of motor fuel subjected to thermo-oxidative cracking.[62]

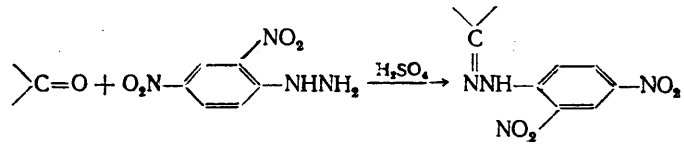
and reliable determination of admixtures of phenols or carbonyl compounds against the background of halogenohydrocarbons, hydrocarbons, or esters.[31] Organic and inorganic acids can be identified in air by a simple and effective method, for example, with the aid of a pre-column with $K_2CO_3$ [71] or with Chromosorb P impregnated with $Na_2CO_3$.[72] An analogous method of determining trace amounts of lower $C_2$–$C_5$ aliphatic acids consists in the use of a preliminary reactor with 2% NaOH on glass beads.[73] After the separation of polar acids from other compounds in the sample, they are concentrated on silica gel, desorbed with water, and then analysed on a chromatograph with a flame-ionisation detector.

A pre-column (6 cm × 5 mm) with glass beads, coated by a mixture of 0.05 g of 2,4-dinitrophenylhydrazine and 0.1 ml of $H_3PO_4$, has been used for the rapid determination of lower aliphatic carbonyl compounds in the waste gases from factories.[74] After the separation of the accompnaying impurities in this type of reactor, the carbonyl compounds were retained in a trap with 25% of 1,2,3-tris(cyanoethoxy)propane on Shimalite cooled with liquid argon to −186 °C. The concentrator was then heated to 120 °C, the sample was desorbed into a chromatographic column 1.5 m long with 5% of the same SLP on Carbopack B, and the toxic impurities were analysed at 70 °C using a flame-ionisation detector. For a reliable determination of phenolic and aliphatic acid microimpurities in air, the same authors[75] used a fore-column (7 cm × 4 mm) with 20% KOH on glass beads (0.6 to 0.25 mm). The presence of the sought compounds in the sample was inferred from the difference between the chromatograms obtained with and without a pre-column, in the latter case the sample being simply removed to a trap with Tenax GC. After the desorption of the enriched sample, the mixture was analysed on a glass column (1.75 m × 3 mm) with 0.1% SP-1000 on Carbopack C at 205–220 °C using a flame-ionisation detector.

**Table 10.** Methods for the identification of chlorohydrocarbons with the aid of the RSM.[3,64–67,79]

| Target components | Sorbent in pre-column | Sorbed impurities |
|---|---|---|
| Chlorohydrocarbons | 5A molecular sieve and conc. $H_2SO_4$ | oxygen-containing organic compounds |
| Chlorohydrocarbons | ditto | hydrocarbons and oxygen-containing organic compounds |
| Chlorohydrocarbons | metal hydrides | oxygen-, nitrogen-, and sulphur-containing compounds |
| Vinyl chloride, trichloroethylene, and tetrachloroethylene | 5A molecular sieve, $H_2SO_4$, and Versamid 900 | hydrocarbons and chlorine- and oxygen-containing compounds |

An interesting problem solved with the aid of the RSM [36] is that of the determination of ethanol impurities in respired air. The aldehydes (especially acetaldehyde) and ketones, which interfere with the determination, can be differentiated by an effective procedure which involves the use of several prechromatographic reactors ($H_3BO_3$; *o*-dianisidine; 2,4-dinitrophenylhydrazine; benzidine or hydroxylamine), which are listed in Table 11. The use of pre-columns with different combinations of the above reagents makes it possible to remove in succession ketones, aldehydes, and alcohols from the mixture analysed, in conformity with the reactions described by the equations[76]



$$RCHO + NH_2OH \cdot HCl \rightarrow RCH{=}NOH + HCl + H_2O\ ;$$

$$H_3BO_3 + C_2H_5OH \xrightarrow{H_2SO_4} (C_2H_5O)_3B + H_2O\ .$$

**Table 11.** The RSM identification of organosulphur impurities.[64–67]

| Target components | Sorbent in pre-column | Sorbed impurities |
|---|---|---|
| Mercaptans | 4A zeolite | $C_1$–$C_3$ hydrocarbons and $C_1$–$C_3$ alcohols |
| Mercaptans, sulphides, and thiophens | Versamid 900 | alkyl halides and aryl halides |
| Mercaptans | poly(vinyl chloride)* | alkylbenzenes, primary alcohols, and amines |
| Sulphur dioxide | $NaHCO_3$ | sulphides, mercaptans, and hydrogen sulphide |

*At 55–75 °C.

These methods make it possible to identify reliably the above compounds in a complex mixture of volatile substances in the respired air.

### 3. Determination of Chloro-Derivatives of Hydrocarbons

The use of the RSM analysis yields satisfactory results in the gas-chromatographic determination of organochloro-compounds, many of which exhibit a pronounced carcinogenic activity, since this procedure makes it possible to detect reliably microamounts of these toxic compounds (for example, vinyl chloride) against the background of the less dangerous accompanying impurities comprising hydrocarbons, oxygen-containing compounds, etc.[30]

A pre-column with sodium bisulphite, which forms a complex with the target compound, is used to separate vinyl chloride from the acetaldehyde, which frequently accompanies vinyl chloride and interferes with its determination.[76,77] Admixtures of light hydrocarbons and oxygen-containing compounds were effectively separated on a pre-column with 5A zeolite and concentrated sulphuric acid on glass wool.[78] Vinyl chloride was analysed at the level of the maximum permissible concentration (0.1 mg $m^{-3}$) on a column with 0.2% of Carbowax 1500 on graphitised carbon black or Polysorb-1 at 50 °C on a chromatograph with a flame-ionisation detector. One should bear in mind that all the procedures (removal of samples onto activated charcoal, desorption of the sample by chlorobenzene, storage of the sample, etc.) must be carried out at a temperature not exceeding 0 °C to avoid losses of vinyl chloride. A chromatogram of a mixture of vinyl chloride and the admixtures interfering with its determination is presented in Fig.10.

An analogous pre-column has been used also to determine other chlorine-containing hydrocarbon impurities in air (tri- and tetra-chloroethylene, chlorobenzene, etc.). After the RSM concentration, these impurities were readily identified by standard chromatographic procedures.[79]

When it is necessary to separate halogen-containing hydrocarbons from compounds of any one class (hydrocarbons, oxygen compounds, etc.), the use of the pre-columns listed in Table 10 gives satisfactory results.

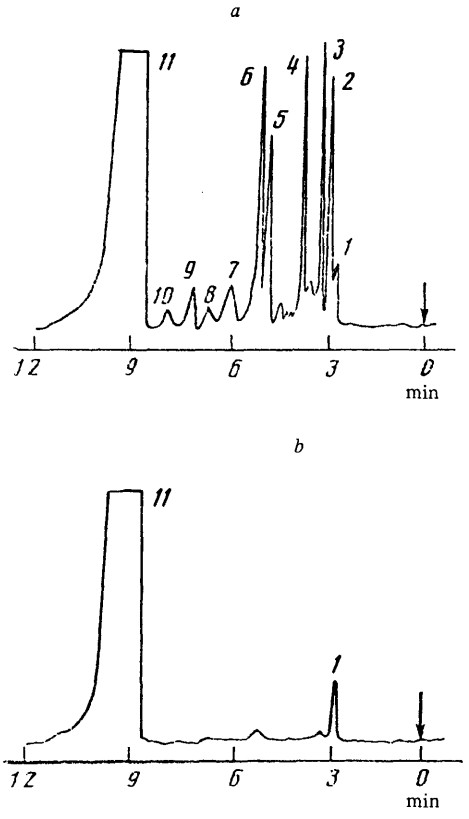



**Figure 10.** Identification of vinyl chloride in a complex mixture of volatile compounds evolved into air on heating artificial leather: *a*) without the use of a pre-column; *b*) beyond the pre-column containing 5A zeolite in sulphuric acid;[78] 1) vinyl chloride; chromatographic peaks *2–10* were not identified; 11) toluene (solvent).

The employment of molecular sieves can lead to the adsorption (up to 8–12%) on the outer faces of the zeolite crystals of the impurities being concentrated, i.e. can lead to additional sorption which is not taken into account.[31] This factor must be allowed for in the interpretation of the results of the identification of impurities using the 5A, 10X, and 13X zeolites as pre-column packing.[3,31,64]

## 4. Determination of Sulphur-Containing Organic Compounds

Sulphur-containing organic compounds, many of which are powerful odorants, are encountered in many petrochemical industries and contaminate the air in the workplace in petroleum refineries.[3]

It has been found that concentration by the RSM is a no-less effective procedure for the identification of organosulphur compounds than the use of flame-photometric and photo-ionisation detectors selective with respect to sulphur.[3,36] The former does not give rise to a significant signal with hydrocarbons but responds to many compounds with functional groups.[80] Although the latter makes it possible to determine picogram amounts of sulphur compounds,[3,40] it gives a signal with alkylbenzenes and certain other hydrocarbons of almost the same magnitude.[81]

In certain instances of practical gas-chromatographic analysis, especially when it is necessary to differentiate mercaptans and sulphides from hydrocarbons, the use of the pre-columns listed in Table 11 yields satisfactory results.

The RSM procedures for the concentration of impurities have proved effective in the identification of sulphur-containinng impurities in air contaminated by the vapour of BR-2 motor fuel[82] and white spirit,[30] in the volatile components of pure rubbers based on natural butyl-rubber,[83] and in the analysis of air from the workplace in petrochemical undertakings.[36,49] A pre-column with $NaHCO_3$ makes it possible to separate microamounts of sulphur dixoide from hydrogen sulphide, mercaptans, sulphides, and disulphides.[84]

## 5. Determination of Nitrogen-Containing Organic Compounds

In this case the RSM analysis is most difficult, because nitrogen compounds are very reactive. It is therefore very difficult to select chemical reagents and sorbents which would absorb the accompanying admixtures (including inert hydrocarbons) and would not react with nitrogen compounds (amines, amides, nitriles, nitro-compounds, lactams, etc.).[3,30,31] Thus a reactor with the 5A molecular sieve and Versamid 900 retains only hydrocarbons, certain oxygen-containing hydrocarbon derivatives, and a reactive halogen compound. Nevertheless, even when only 40–50% of all the admixtures interfering with the analysis are removed with the aid of this pre-column, we may hope for an appreciable increase in the reliability of the subsequent gas-chromatographic identification of the nitrogen compounds.[30,36]

**Table 12.** The RSM identification of nitrogen-containing organic compounds.[3,30,65]

| Target components | Sorbent in pre-column | Sorbed impurities |
|---|---|---|
| Amines | $H_3BO_3$ | alcohols and phenols |
| Amines | 2,4-dinitrophenylhydrazine | aldehydes and ketones |
| Amines | zinc oxide | carboxylic acids, alcohols, and phenols |
| Amines | KOH | carboxylic acids, phenols, cresols, ethers, and esters |
| Nitrogen-containing compounds | Versamid 900 and silver nitrate | halogen-containing hydrocarbons |

In certain cases, for example, those listed in Table 12, concentration by the RSM yields entirely satisfactory results. These procedures have been used in analytical practice for the analysis of air contaminants, for the identification and determination of amines in the gases evolved from rubber articles,[36,49] and in the elucidation of the composition of the volatile substances released into the air of the workplace in the manufacture of polymers and their processing.[3,30,36]

A pre-column with glass wool or a glass filter impegnated with [(4-nitrophenyl)methyl]propylamine has been used for the identification and quantitative determination in air of trace concentrations of aminocarbonyl derivatives of toluene.[85]

A method involving the preliminary removal of nitrites by ion exchange and denitrosation with the aid of sodium iodide or sulphanilamide is used for the determination in the air of the workplace in industrial undertakings of admixtures of *N*-nitroso-compounds (formed from anticorrosion additives to lubricating-cooling liquid compositions).[86] For the correct identification in air of microamounts of *N*-nitroso-compounds, which eliminates the interfering influence of amines (precursors of *N*-nitroso-compounds), one uses in sampling a two-section cartridge with sulphamic acid for the absorption of amines in the first section and a mixture of sulphamic acid with magnesium silicate for the trapping of *N*-nitroso-compounds in the second section. After sampling, the contents of the second section are desorbed with acetone and analysed by gas chromatography.[87]

### 6. Determination of Inorganic Compounds

The reaction-sorption concentration method has been used successfully also in the determination in air of trace amounts of toxic inorganic substances.[3,21,30,34,40] In order to determine nitrous oxide, air is initially freed from the $H_2O$ and $CO_2$ impurities, which interfere with the analysis, by passing the sample through a pre-column containing anhydrous $CaSO_4$, $Mg(ClO_4)_2$, and Ascarite.[88] The column with 13X zeolite retains irreversibly the $NO_2$ and $N_2O$ impurities, but it is possible to separate on it $O_2$, $N_2$, and NO;[33,89] this enables one to achieve the preliminary separation of the reactive nitrogen oxides, whose separate determination has always constituted a difficult problem.[21,34,40]

In order to eliminate the mutual influence of inorganic gaseous impurities, a thin-fibre polystyrene filter, containing iron chelate compounds, is employed. The concentration of the $NO_2$, $NH_3$, $H_2S$, and $SO_2$ impurities in air after it has been passed through such a filter at a rate of 0.1 litre $min^{-1}$ diminishes by a factor of ~50 compared with the initial concentration.[90] In order to separate the highly reactive sulphur trioxide, which tends to polymerise, from one of the most important contaminants in air, namely sulphur dioxide, the air to be analysed is passed through an absorber containing 97%[91] or 100%[92] sulphuric acid, which effectively absorbs $SO_3$. The influence of $SO_2$, which interferes with the gas-chromatographic determination of $H_2S$ microimpurities, can be eliminated by a preliminary step in which the air to be analysed is passed through a tube filled with glass beads treated with $Na_2SO_3$. In the subsequent chromatography of the sample on a column with Porapak Q at 100–200 °C, it was possible to determine selectively an admixture of $10^{-7}$% of hydrogen sulphide in air over various regions of the Atlantic Ocean.[93]

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The hybrid reaction-sorption method, based on the simultaneous employment of chemical subtraction and sorption concentration methods, makes it possible to increase significantly the reliability and reproducibility of the identification of impurities in complex mixtures of air contaminants. The application of the RSM has greatly expanded the field in which gas chromatography can be used to determine organic and inorganic impurities in air (and in various gaseous media). The employment of the RSM concentration of impurities in their determination in various liquids (solvents, natural and waste water, brines, technological water, etc.) is undoubtedly also promising.

The reaction-sorption method is universal and can be used in combination with any analytical procedure (chromatographic, spectroscopic, electrochemical, etc.). The application of the RSM improves almost all the metrological characteristics of the methods for the determination of impurities (selectivity, detection limits, reliability, reproducibility, etc.) and expands the range of the active methods and procedures available in analytical chemistry.

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# The Forms of Trace Elements in the Abiotic Phases of Natural Aqueous Media

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The literature data on the phase, physicochemical, and chemical properties of trace elements (microelements) in the abiotic phases of natural aqueous media—the atmosphere, the surface microlayer of water, natural waters, suspended and colloidal particles, bottom deposits, and pore waters, as well as the mechanisms of the interconversions of these forms are surveyed and critically examined. The ways in which trace elements are absorbed and removed via the interfaces of these phases and on mixing in the estuary as well as the causes of such sorption and removal are considered. It is shown that the form of the trace elements in the phases of all types of natural waters (in oceans, seas, rivers, estuaries, lakes, and bogs) plays a decisive role in their transport, biological availability, and biogeochemical cycles.
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## I. INTRODUCTION

In many industrially developed countries the present degree of pollution of individual internal water basins and regions of coastal sea waters by chemicals of anthropogenic origin exceeds the ecologically safe level. Together with organochlorine compounds and petroleum, the toxic elements Hg, Pb, Cd, As, Cu, Se, as well as others whose concentration in natural waters (NW) is less than 1 mg $kg^{-1}$ (1 p.p.m.) constitute a special danger. They are referred to as trace elements (TE) and they do not include biogenic and radioactive elements or dissolved gases.

The determination of such extremely low TE concentrations in natural aqueous media constitutes an extremely difficult analytical problem. The situation is greatly complicated by the fact that at any stage of the analysis, especially in the removal and preliminary treatment of samples, it is very easy to contaminate the latter from the sampler, air, reagents, the vessels used, and other sources. This is particularly important for ocean waters, in which the concentration of many TE is lower by several orders of magnitude than in surface waters and can amount to 1 ng $kg^{-1}$ (p.p.t.). As the above causes of the contamination of samples in analysis have been eliminated and the sensitivity and selectivity of the analytical methods for the determination of TE have improved, their measured content in NW, including ocean waters, has steadily decreased during the last decade, by orders of magnitude despite the constantly increasing anthropogenic injection of TE into NW. However, this trend has been sharply retarded in recent years and the concentrations of many TE established at present, even in ocean waters,[1,2] may be regarded as sufficiently reliable. They will be quoted below in the appropriate sections. However, the main bulk of the data concerning the content of the TE in sea waters, published up to 1975,[1] and in river waters, probably up to 1973, must be rejected.

However, the overall content of TE in aqueous media still does not reflect the true degree of pollution of the latter. Studies in various countries of the causes of numerous instances of the poisoning of hydrobionts by TE made it possible many years ago to reach the important conclusion that the biological accessibility and toxicity of TE depends very greatly on the form in which they exist. The data accumulated at the present time also permit the assertion that the forms in which TE exist plays a decisive role in their transport in the biogeochemical cycle. The knowledge of the form in which TE exist in aqueous media has therefore assumed first class importance.

Two main approaches are used to study the forms in which TE exist in NW. The first is theoretical and involves the calculation of the equilibrium concentrations of all the dissolved forms with the aid of mathematical models based on the employment of the experimental concentrations of TE and ligands as well as the published stability constants of the TE–ligand bonds. Chemical modelling embraces at the present time all possible competing equilibria; computer programs are employed for thermodynamic calculations. The accuracy of the computer modelling is however greatly reduced as a consequence of the uncertainty of the published stability constant and activity coefficient data. Furthermore, many parameters influencing the forms in which TE exist are not as a rule included in the calculation in view of the lack for the majority of them of qualitative and quantitative data concerning the pH, the redox potential, the nature of the vast majority of organic ligands, colloidal particles and the adsorption on them, the interfacial precipitation reactions, dissolution and sorption, biological and physical processes, etc. These factors as well as the lack of information about the non-equilibrium conditions which exist in many NW yield calculated results which are extremely doubtful. The advances in the field of chemical modelling have been described elsewhere.[3-6]

Another approach to the study of the forms of TE is analytical. All the experimental forms of TE in the abiotic phases of natural aqueous media can be usefully divided into three large groups—the phase, physicochemical, and chemical forms. The particular phase form to which the TE belongs is determined by the principal phases of aqueous media in which the TE is present—the natural atmospheric layer, the surface microlayer (SML) of water, NW, suspended and colloidal particles, deposits in aqueous media, and pore waters. A classification based on the physicochemical forms depends on the presence of the TE in specific fractions of aqueous media (for example in the dissolved organic fraction, the suspended inorganic fraction, and the sorbed fraction), which are subdivided either in terms of their size (established, for example, by ultrafiltration and gel filtration) or in terms of the lability of the fraction in relation to the analytical technique employed (for example, ion exchange or inversion voltamperometry are used for this purpose). The chemical forms can exist in aqueous media as compounds of TE in various oxidation states [for example inorganic arsenic(III) and arsenic(V)], as organoelemental compounds (for example, MeHgCl and $Bu_2SnMe_2$), or as complexes (for example, vitamin $B_{12}$). In this classification the chemical forms of TE are frequently their physicochemical forms; the overall amount of TE in these forms yields the overall content of TE in each phase of natural aqueous media.

The distribution of TE and their forms in the phases of aqueous media enumerated above takes place via very complex pathways as a result of various chemical, physicochemical, physical, and biological processes, the mechanisms of which are still little understood. The available chemical data and phenomenological models do not permit the prediction of the distribution of TE, let alone their forms, between different phases of aqueous media, which constitute extremely complex systems usually possessing variable qualitative and quantitative compositions.

The analytical determination of the forms of TE in NW cannot be regarded as a problem which has been solved, firstly, owing to their extremely low concentrations and, secondly, owing to their sensitivity to the salt composition, pH, the content of dissolved organic and high-molecular-weight compounds, colloidal and suspended particles, and other conditions which depend both on the type of the NW and on the time of year. It is important to note that the equilibrium concentrations of different forms of TE in NW inevitably change when samples are taken, as a consequence of their contact with atmospheric oxygen and the walls of the sampler and changes in temperature and pressure, and also in the course of their separation (isolation) and analysis. These changes are indefinite, but it is essential to minimize them in all cases. A number of reviews have been published on the methods for the determination of the physicochemical[3,7–14] and chemical[7] forms of TE in NW.

The aim of the present review is to examine the phase, physicochemical, and chemical forms of TE in the abiotic phases of natural aqueous media—the atmosphere, the SML, NW, suspended and colloidal particles, deposits in aqueous media, and pore waters, and also the mechanism of their interconversions. Individual aspects of this question were discussed earlier in relation to TE,[15] Hg, Cd, and Zn,[16] Cd in sea water,[17] organoelemental compounds,[18,19] and TE in ocean waters.[20] The types and causes of the absorption removal of different forms of TE through the interfaces of the above phases and in estuarine mixing are also examined.

In view of the existence of the above problems in the analytical determination of TE and their forms in aqueous media, we shall consider here, with rare exceptions, only data published during the last 5–7 years. Owing to the limited size of the article, they will be only briefly described and many publications concerned with the topic under discussion will not be mentioned. Preference is given to the latest, fundamental information and also review articles.

## II. THE ATMOSPHERE

The substances present in the atmosphere in the liquid (water), solid (aerosols), and gaseous states exist in variable concentrations. Among them impurities of natural origin include particles of sea salts, dust from active volcanoes and continental erosion, etc. while anthropogenic impurities comprise different types of smoke and gases ejected by industrial undertakings, automobile transport, etc. The chemical composition of aerosols and atmospheric deposits has assumed great importance both for the investigation of the pollution of the environment on a global scale and for the determination of their role in the establishment of the chemical composition of NW.

It has been shown that Hg, Pb, Cd, Se, Sb, and other TE are transported in the atmosphere over long distances above the oceans.[21] The content of these TE exceeds by 2–3 orders of magnitude their average concentration in the Earth's core. This applies, for example, to the aeolian suspension over the pelagic regions of the Atlantic Ocean,[22] but the latter has, however, a different origin.[23]

In the marine aerosols, whose content varies in the range 0.003–30 μg $m^{-3}$,[24] many TE have been determined.[21–24] For example, the concentrations of Cr and Se over the Atlantic Ocean are 0.54 and 0.033 mg $m^{-3}$ [24] and those of Pb are 0.98 and 0.15 mg $m^{-3}$ in the southern and northern hemispheres,[25] whereas over the Pacific Ocean the concentrations of these TE are respectively 0.73, 0.028,[24] and 0.2 mg $m^{-3}$.[26] It is noteworthy that the TE in natural marine aerosols exist preferentially in the water-soluble, exchangeable, and weakly bound forms.[24]

The content of the TE and their forms in rain water and in the gas phase has been studied to a lesser extent than in aerosols. The following amounts of TE have been observed in rain water (ng $litre^{-1}$): Hg 2 (open ocean),[27] Cd 320 (Lake Michigan),[28] Se(IV) 52.4 and Se(VI) < 5 (California),[29] As(III) < 2, As(V) 13.7, $MeAsO(OH)_2$ < 2 and $Me_2AsO(OH)$ 12 (California),[30] As(III) 214 and As(V) 4850 (Belgium),[31] Ge(IV) 0.5–0.7, $Me_2Ge$(IV) 1.0–5.9, and $Me_3Ge$(IV) 0.2–1.0 (Florida),[32] Sn(IV) 11, MeSn(IV) 5.9, $Me_2Sn$(IV) 7.4, and $Me_3Sn$(IV) 0.22 (Florida),[33] $Me_nEt_mPb$(IV), ($n$, $m$ = 0–3) < 2–68 (Belgium),[34] Hg (inorganic) and Hg (organic) 12.2 and 0.8 respectively (Japan),[35] and Pb (inorganic) 133 × $10^3$ and 280 × $10^3$ [Antwerp, Belgium, suburbs and city centre respectively (Translator)].[34]

The fraction of mercury in the gaseous form corresponds to more than 99% of its entire content in the atmospheric forms in the natural atmosphere over the sea.[27] In the northern and southern hemispheres its concentrations in the pure atmosphere over the sea are respectively ~1.5 and ~1.0 ng $m^{-3}$,[27,36] ~10% being present in the form of $Me_2Hg$.[36] About 50% of the mercury in the coastal sea atmosphere may be present in the organic form.[27] Data concerning the formation and fate of volatile molecular forms of TE have been surveyed.[37]

There is a constant reciprocal transfer of TE through the ocean–atmosphere interface, which are thus involved in the establishment of the chemical composition of both phases. The direction and rate of transfer are determined by the forms of the TE. The estimates of the fluxes for different TE and different regions of the world ocean can

differ markedly. Rains, which carry TE in a water soluble form, apparently play the greatest role in the atmospheric transport of TE to the ocean. It has been suggested[38] that, up to a depth of 100 m in the North Atlantic waters, 100% of Pb, 50% of Zn, Cu, and Mn, and up to 25% of Cd, Cr, and Al and other TE are of atmospheric origin. This has been demonstrated for Mn[39] and has been postulated for Se and Bi.[40] The atmospheric input of Pb has been studied in particularly great detail.[25,26,41,42] For example, it has been calculated that 24% of the lead entering the atmosphere annually is deposited on the ocean surface of the North Atlantic region.[25]

However, the exact sources of the TE brought through the atmosphere remain obscure. In certain regions of the world ocean Pb, Ni, Cu, and Zn are probably to a large extent of anthropogenic origin. They are formed, for example, by combustion of mineral fuels.[38,43] However, according to Jaworowski et al.,[44] the natural input of Pb, Hg, and Cd, for example, with atmospheric dust and products of volcanic eruptions, is of decisive importance.

The transfer of TE from the surface of the ocean to the atmosphere takes place as a result of wind action; TE are contained in the air bubbles bursting on the surface of the ocean and in the vapour. It has been observed that Cu, As, Hg, Pb, and other elements are mainly concentrated in the submicron fraction of sea aerosols,[23] in the establishment of the chemical composition of which the SML plays a major role, the latter being usually greatly enriched in TE compared with the bulk of the sea water (see Section III).

It has been suggested that considerable amounts of certain TE, particularly those forming gaseous methyl derivatives in the marine medium (Hg, As, Pb, etc.), pass from the surface of sea water to the atmosphere, since otherwise it would be impossible to balance their global cycles.[23,24] This can be regarded as proved for mercury.[27]

## III. THE SURFACE MICROLAYER ON WATER

Studies in recent years have demonstrated that extremely important chemical and biological processes occur on the surfaces or at the interfaces of different NW phases. The latter include the interface between the ocean and the atmosphere—the SML, which is the site where many substances of natural and anthropogenic origin are concentrated (TE, petroleum and chlorinated hydrocarbons, detergents, etc.) as well as the habitat of a varied and abundant flora and fauna (neuston) with a much higher biological activity than in the lower water layers. The marine SML with its enormous size plays an especially important role. A series of reviews on chemistry and biology have been devoted to it.[45,46]

The physical stability of the SML is ensured by surface tension forces and by the presence of organic films. At the same time it is a climatically unstable medium subjected to much greater oscillations in temperature and salinity ($S$) than the subsurface water layer. In order to explain the available facts, a model has been proposed,[45] according to which the upper layer of the marine SML consists of a unimolecular lipid film 10–20 Å thick, below which there is a polysaccharide protein layer 100–300 Å thick and a layer, closely linked to it, of abiotic suspended matter of bacterioneuston, yeast, and mould (to a depth of ~1 μm). In marshes (saline bogs near the sea) two types of SML have been observed.[47] The commonest of these is opaque and is enriched in organic matter, while the second type encountered much more rarely, has a bluish colour and is enriched in iron.

Various SML serve simultaneously as sources and traps for substances in the atmosphere and in bulk water. The methods whereby TE and their forms are transferred in the ocean–atmosphere system have been described in Section II. They pass from the bulk of the water to the SML as a result of upwelling, convection, diffusion, and bubble flotation.

In the SML of all types of NW the concentrations of TE (Pb, Cu, Cd, etc.) and their forms are usually much higher than in the subsurface water layers. This has been demonstrated for lake,[48] river,[49] marsh,[50] and sea[43,51] waters. The above difference is especially large for the bound dissolved[49] and suspended[48] forms of TE. Their concentrations can differ by an order of magnitude and more [differences in concentrations reaching 4 orders of magnitude have been observed for $Bu_3Sn(IV)$, $Bu_2Sn(IV)$, and the total Sn in various NW of Canada[52]], which reflects a much higher content of suspended materials and of dissolved organic material in the SML compared with the bulk water. Although the forms of TE in the SML and their exchange with the bulk water and with the atmosphere are controlled by a series of processes which are not yet fully understood, it appears likely that the most important of these are surface adsorption on the suspension and complex formation involving the dissolved organic substance. The influence of a surface-active dissolved or colloidal organic substance on the chemical form and transport of Pb, Cu, and Hg through the marine SML has been discussed.[53] A decrease of the Fe and Mn contents in the SML as a consequence of the precipitation of the mineral particles carrying them[43] as well as the lack of enrichment by basic ions (K, Mg, Ca, Cl, and Br) have been observed.[51]

It is essential to note that many fundamental questions associated with the SML, including the entry, redistribution, and fate of TE and their forms have been clearly inadequately investigated. For example, the relative contribution of aerosols and bubble flotation to the enrichment of the marine SML by suspended TE remains obscure. According to some data,[43] they are approximately the same, while according to others, flotation predominates.[54] Furthermore, the lack of generally adopted samplers and methods for taking SML samples whose depths may differ by several orders of magnitude in the work of different investigators[45] makes it very difficult and sometimes even impossible to compare the experimental results.

## IV. NATURAL WATERS

### 1. The Overall Content and Distribution of TE

As already noted above, the major advances in analytical chemistry during the last ten years and the elimination of contamination at all the stages of the analysis[2,55,56] made it possible to demonstrate that the concentration of the majority of TE in unpolluted ocean waters are in fact lower by 1–3 orders of magnitude than had been believed previously.[1,2]

The present data about the concentrations of all the elements in the Periodic System in open ocean waters have been compiled in two publications.[1,57] The first indicates for each element the proportions of inorganic forms in oxidised sea water calculated as described by Stumm and Morgan[4] and Turner et al.,[5] the range and average values of the concentrations, and the type of distribution and the the second gives the concentrations in the surface and deep (~1000 m) waters and predicts the average concentrations, the type of distribution, and the relation to the chlorine content. Table 1 lists the concentrations and types of pollution of the most important TE.[1]

It has been suggested that the vertical TE profiles be subdivided into 7 main types depending on the characteristics of the processes controlling them:[1] (1) the conservative type, which corresponds to the case where the concentration of the TE is independent of the salinity as a consequence of their low reactivity in sea water (this has been observed, for example, for Pb, Cs, and $MoO_4^{2-}$); (2) the biogenic type, in which the surface layers are depleted and the deep layers are enriched in trace elements as a result of their involvement in the biogeochemical cycle: the TE are removed from the surface layers of water by the plankton and the biological suspended particles formed, which descend to deeper regions, where the TE are regenerated via their oxidation or transition to a soluble state (for example, Cd, Zn, Se, and Ni); (3) surface enrichment and depletion in deeper regions when TE enter the upper layers of water (for example, from the atmosphere and rivers) and are then rapidly and constantly removed from the water (for example, Pb and Mn); (4) the minimum TE concentrations occur at an intermediate depth when TE fall on the surface of the ocean and are regenerated near its bottom, or are scavenged (adsorption on submerging particles) during passage through the bulk of the water (for example, Al and Cu); (5) the maximum TE concentration occurs at an intermediate depth due to hydrothermal activity (for example, Mn); (6) the minimum or maximum TE concentration occurs at an intermediate depth within incompletely oxidised layers associated with the occurrence of reductive processes in the bulk of the water or deposits on the adjoining continental slope [for example, Mn(II), Fe(II), and Cr(III)]; (7) the maximum or minimum TE concentration occurs in oxygen-free waters, established as a result of the interconversion of the $SO_4^{2-}$–$H_2S$ air [for example, Mn(II), Fe(II), and Cr(III)].

Table 1. The concentrations and type of distribution of TE in ocean water.[1]

| Element | Concentration, nmol $kg^{-1}$, for $S$ = 35%* | | Type of distribution |
|---|---|---|---|
| | range | mean | |
| Ag** | (0.5—35) | (25) | biogenic |
| Cd | 0.001—1.1 | 0.7 | » |
| Cr | 2—5 | 4 | » |
| Ni | 2—12 | 8 | » |
| Zn | 0.05—9 | 6 | » |
| Ge** | ≤7—115 | 70 | » |
| As | 15—25 | 23 | » |
| Se | 0.5—2.3 | 1.7 | » |
| Be** | 4- 30 | 20 | biogenic and scavenging |
| Cu | 0,5—6 | 4 | ditto |
| Al | (5—40) | (20) | minimum at intermediate depth |
| V | 20—35 | 30 | weak surface depletion |
| Mn | 0.2—3 | 0.5 | depletion in deep regions |
| Fe | 0.1—2,5 | 1 | depletion on the surface and in deep regions |
| Co | (0.01—0.1) | (0.02) | ditto |
| Pb** | 5—175 | 10 | high content in surface waters, depletion in deep regions |
| Sn** | (1—12) | (~4) | high content in surface waters |
| Sb | (1.2) | — | not established |
| Ti | (<20) | — | ditto |
| Au** | (25) | — | » |
| Hg** | (2—10) | (5) | » |

*The round brackets show that the data are unreliable.
**The concentrations are given in pmol $kg^{-1}$.

In addition to the data quoted by Bruland,[1] vertical profiles have also been described for Ni, Cu, and Cd,[58,59] Zn,[58] Co,[60] Ag,[61] Fe,[62] Pb,[42] Hg,[63] Cr,[64,65] Mn,[66] V,[67] and the lanthanides.[68]

It is essential to note that concentrations of TE differ markedly in different oceans[2,55,69-71] as a consequence of the differences between the hydrographic parameters, biological productivity, and atmospheric input. The data for the same ocean obtained by different investigators[2] also show discrepancies due to the lack of a single methodological approach to the determination of TE. This has been confirmed by the comparison of different samplers[2,72] and analytical methods[73] and also by intercalibrations.[74]

The concentrations of TE in epicontinental seas and coastal waters are usually higher than in the open regions of the oceans (Table 2). We may also note data for the content of Hg (ng $litre^{-1}$) in the Sea of Japan (4.8[80] and 16.7[81]), the Sea of Japan [near the middle part of the mainland of Japan] (6.3 and 12.4),[81] the Bering Sea (5.8), the East and South China Seas (5.2),[80] and in the coastal waters of the USA (0.2–1.0[82] and 12.7[83]) and Japan (2.9—12.5),[84] and the content of Cr in the Sea of Japan (~0.45 μg $litre^{-1}$)[85] and of Co in the San Francisco Bay (0.05–1.2 μg $litre^{-1}$).[60] A comparative study of the distribution of TE in oceans and coastal waters has been carried out.[71]

Table 2. The concentrations of TE in epicontinental seas and coastal waters (μg $litre^{-1}$).

| Region | Cd | Cu | Mn | Ni | Pb | Zn | Refs. |
|---|---|---|---|---|---|---|---|
| Baltic Sea | 0.027 | 0.661 | 0.341 | 0.810 | 0.016* | 0.922 | [75] |
| North Sea | 0.033 | 0.925 | — | — | 0.148 | — | [71] |
| Mediterranean Sea | 0.008 | 0.090 | — | — | 0.035 | — | [76] |
| Red Sea | 0.005 | 0.090 | — | — | 0.013 | — | [71] |
| Sargasso Sea | 0.0002 | 0.08 | 0.13 | 0.12 | — | 0.004 | [70] |
| Gulf Stream | 0.017 | 0.16 | — | 0.23 | — | — | [69] |
| Shelf waters of the USA | 0.022 | 0.25 | 1.15 | 0.33 | — | 0.16 | [70] |
| Bermuda platform | 0.047 | 0.2 | 0.19 | 0.14 | 0.15 | 0.3 | [77] |
| Gulf of Mexico | 0.022 | 0.57 | — | 0.53 | — | — | [78] |

*Taken from Danielsson and Westerlund.[79]

Table 3. Concentrations of dissolved TE in rivers (μg $litre^{-1}$).

| River | Fe | Mn | Cr | Zn | Ni | Cu | Cd | Refs. |
|---|---|---|---|---|---|---|---|---|
| St. Laurence | 55 | 6.3 | — | 8.6 | 1.5 | 2.5 | 0.11 | [86] |
| Mississippi | 10 | 10 | 0.3 | — | 1 | 2 | 0.1 | [87] |
| Amazon | 2.0 | 19 | 2.0 | — | 0.27 | 1.8 | — | [88] |
| Yukon | 50 | 20 | 2.3 | — | 0.43 | 2.0 | — | [88] |
| Hudson | 32 | 1.5 | — | 4.6 | 1.9 | 3.2 | 0.20 | [89] |

The contents of dissolved TE in certain rivers are listed in Table 3. It is important to note that the majority of the TE are bound to a suspension (see Section V). In tropical rivers during the monsoon period, the concentrations of TE can decrease by a factor of several tens.[90] The average content of Hg is ~20 ng $litre^{-1}$ in ten rivers of the USA,[83] 4.3–21.1 ng $litre^{-1}$ in the surface waters of Japan,[35,91] 9.8 ng $litre^{-1}$ in the River Thames,[92] and 6.6 ng $litre^{-1}$ in the Ottawa River and 26.2 ng $litre^{-1}$ in the Suimon River.[93]

## 2. The Physicochemical Forms of TE

Dissolved TE can be present in NW as part of the composition of the various physicochemical forms differing in their dimensions (Table 4). Several general schemes for the determination of these forms of TE have been proposed,[7,10] differing in the analytical methods employed and also in the procedures used for separation and decomposition.

Table 4. The possible physicochemical forms of TE in NW and their dimensions.[10]

| From | Example | Approximate size, μm |
|---|---|---|
| Suspended | — | >0.45* |
| Simple hydrated ions of elements | Cd (II) $(H_2O)_6$ | 0.0008 |
| Simple inorganic complexes | Pb $(H_2O)_4Cl_2$ | 0.001 |
| Simple organic complexes | Cu glycinate | 0.001—0.002 |
| Stable inorganic compounds | PbS, $ZnCO_3$ | 0.001—0.002 |
| Stable organic complexes | Cu fulvate | 0.002—0.004 |
| TE adsorbed on inorganic colloids | Cu (II) — $Fe_2O_3$; Pb (II) — $MnO_2$ | 0.01—0.50 |
| TE adsorbed on organic colloids | Cu(II)-humic acid | 0.01—0.50 |
| TE adsorbed on mixed organic and inorganic colloids | Cu(II)-humic acid/$Fe_2O_3$ | 0.01—0.50 |

*It is retained on a filter with a pore size of 0.45 μm.

It must be emphasised that the dissolved organic matter, the main bulk of which (up to 80%) consists of highly oxidised biologically stable high-molecular-weight compounds, resembling the humic substances (HS) isolated from soil, play the main role in the distribution of the dissolved physicochemical forms. The rest of the organic matter consists of a mixture of polypeptides, polysaccharides, aminoacids, aliphatic acids, hydrocarbons, vitamins, and other compounds whose extremely low concentrations (usually less than $10^{-6}$ M) create serious analytical difficulties in their identification. The role of organic matter in river[94] and sea[95,96] waters has been examined in detail.

The exact structure of aqueous HS is unknown. They are high-molecular-weight polyelectrolytes of variable composition.[97,98] On the basis of chemical and spectroscopic data, it is believed that[98] marine fulvoacids and humic acids (HA) are structurally very similar, differing mainly by the absence of aromatic character in the former, and consist of cross-linked auto-oxidised polyunsaturated aliphatic acids.

The mechanism of the chemical binding of TE ions by HS is unknown, but it is believed that this interaction takes place via the formation of complex bonds of different types as a result of ion exchange, surface adsorption, and chelation.[99–101] The role of the HS is significant in the formation of complexes by TE, especially Hg, in surface waters,[102,103] but is much smaller in ocean waters (for example, for Cd, Pb, and Zn[104]), which can be accounted for by the different concentrations of the HS in these waters.

The specific organic forms of the TE in NW, with the exception of the vitamin $B_{12}$, chlorophylls, and a series of chemical forms, cannot currently be determined due to their extremely low concentrations. For this reason one either finds the overall content of the organic forms of TE or one analyses fractions with a specific molecular weight (MW). It is noteworthy that the great variety of methods for the determination of these forms of TE (with or without their isolation from the sample) greatly hinders the comparison of the results obtained by different investigators. Organic forms of different TE in sea water[53,105–109] and surface waters[110] have been observed.

These forms have been investigated in greatest detail for Cu, Hg, and Cr. It has been shown that, among the dissolved forms, the organic Cu fraction can amount to between 3 and 98% in marine waters[53,105–109,111–115] and 50% in surface waters.[116] On the basis of the analysis of EPR spectra, it has been suggested[117] that Cu is bound in these complexes to various reaction centres of the ligand via oxygen atoms. Mercury in the bound state amounts to 4–50% in sea water[53,63,83,84] and 27–100% in surface waters.[35,83,118] The vertical distribution of various forms of mercury in ocean waters is illustrated in Fig.1.[63] The following elements can exist in the organic form in sea water: Cr—45–60%,[85] Fe—12%, Mn—11%,[106] and Ni—up to 8%;[107] Se is present in the organic form to the extent of 40–60% in NW[119] and Pb is present in the organic form to the extent of 20–80% in river and estuary waters.[120] It is noteworthy that usually the highest concentrations of many TE are present in the organic fraction with MW = $10^3$–$10^4$ (see, for example, Refs.63, 121, and 122). The role of organic matter in the binding of TE in NW[99,100] and the methods for the determination of the complexes formed,[3,7,10,123,124] as well as problems concerning the measurement of the complex-forming capacity and of the conventional stability constants for the ligands in NW[125] have been considered.

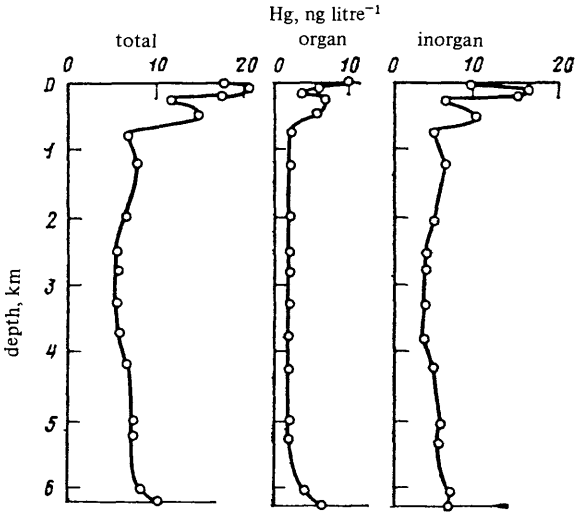



Figure 1. Vertical distribution of the different forms of mercury in the north western part of the Pacific Ocean.[63]

Among other dissolved physicochemical forms of TE, mention should be made of a labile form to which the free ion of the elements and labile complexes are usually assigned.[7,10] The concentrations of the labile mercury are 0.1–0.5 ng litre$^{-1}$ in the Pacific Ocean[82] and 6–60 ng litre$^{-1}$ in the North Sea.[126] The proportion of this form may correspond to the main bulk of the Mn in the <0.015 μm fraction in surface

waters.[127] The labile form is subdivided in its turn into the very labile, moderately labile, weakly labile, and inert forms.[128,129] This specification, which has a kinetic base, can be useful in the study of the biological accessibility of TE. It has been shown that Cd and Zn exist in river waters in more labile forms than Cu and Pb.[128] Overall, only a small proportion of the overall content of TE in NW corresponds to the labile fractions.

The forms of TE and their concentrations can vary greatly in oxygen-free deep waters, which exist, for example, in the Black and Baltic Seas and the fjords of Canada and Norway. The study of the vertical profiles of the dissolved TE in the Baltic Sea has shown that, on passing through the $O_2$–$H_2S$ interface (the anoxic wedge), the Fe, Mn, and Co concentrations increase by a factor not less than 100 and there is a simultaneous increase of the Cu concentration by a factor not less than 100 and Zn, Cd, and Ni concentrations by a factor of 3–5 compared with oxidised waters.[130] The solubility of many TE is then controlled by the formation of disulphide and polysulphide complexes and the elements themselves exist in reduced forms, for example, Cu(I), Fe(II), and Mn(II). The Mn,[131,132] Fe, and Cr[131] redox cycles were investigated previously and it was shown, in particular, that the dissolved Mn(II) accumulates in deep anaerobic waters as a result of the reduction of the suspended $MnO_2$ when it is submerged via the anoxic wedge.

### 3. Chemical Forms of TE

The chemical forms of TE in SW have come to be determined only recently and a limited range of TE in different oxidation states (Cr, As, Sb, Se, and V) have now been investigated. It is noteworthy that the forms in the highest and lowest oxidation states predominate for each of the above TE in the oxidised and reduced SW respectively.

In sea and surface waters the concentration of inorganic Cr(VI) have been found to be 0.1–1.0 μg litre$^{-1}$ [65,133–135] and 0.05–3.75 μg litre$^{-1}$,[133,136] while those of inorganic Cr(III) are 0.002–1.0 μg litre$^{-1}$ [65,85,133,135] and 0.20–2.36 μg litre$^{-1}$.[136] Vertical profiles have been obtained for these forms in ocean waters[64,85] and it has been shown that dissolved oxygen oxidises Cr(III) to the thermodynamically more stable Cr(VI), $MnO_2$ being a powerful catalyst of this process.[137] However, the ratio of the oxidised and reduced forms is not very well understood; it is believed that it is probably controlled kinetically.[138]

The following forms of As[30,31,139–143] and Sb[143–146] have been found in various types of SW (the two elements are designated by the general symbol E): E(III), E(V), MeE(V), and $Me_2E(V)$. Among the inorganic forms, E(V) predominates in the oxidised waters, while in the reduced waters the main form is E(III) and a sharp change in the ratio E(III)/E(V) is observed on passing the anoxic wedge,[143,147] owing to the reduction of E(V) and the possible formation of thiocomplexes.[143,146] In oxidised estuary waters, pronounced seasonal variations in the concentrations of the As forms have been noted;[142] in particular As(III) and the methyl forms of As are absent during the cold months at water temperatures below 9–12 °C probably owing to the sharp decrease of natural biomethylation.

The MeE(V) and $Me_2E(V)$ forms are encountered throughout the photic zone in the oceans but their proportion is only ~10% of the total content of the corresponding dissolved TE.[141,145] The vertical profiles of the chemical forms of As, Sb, and Ge in the Baltic Sea (where the anoxic wedge is at a depth of 170 m) (Table 5)[143] are controlled by biogeochemical cycles.

The concentrations of inorganic Se(IV) and Se(VI), which increase with the depth in the oceans, are in the range 4–64 and 40–120 ng litre$^{-1}$ respectively.[148,149] In the oxygen-free sea water Se(-II) has been detected mainly in the form of Se-aminoacids and (or) peptides with the Se–C bond.[150] It has been shown that Se(IV) and Se(VI) are present in greater amounts in sea water than in surface water;[29,151] the opposite assertion is valid for Se(-II,0).[151] Among the different forms of vanadium, V(IV) and V(V) have been determined in river waters.[152]

Table 5. The vertical profiles of the chemical forms of As, Sb, and Ge (nmol litre$^{-1}$) in the Baltic Sea (the Gotland Depression).[143]

| Depth, m | MeAs | $Me_2As$ | As (III) | As (V) | MeSb |
|---|---|---|---|---|---|
| 10 | 0.43 | 2.79 | 1.44 | 3.12 | 0.032 |
| 40 | 0.23 | 0.20 | 0.18 | 8.46 | 0.030 |
| 100 | 0.04 | 0.07 | 0.11 | 11.6 | 0.022 |
| 150 | <0.04 | 0.07 | 0.18 | 13.2 | 0.019 |
| 175 | 0.06 | 0.15 | 12.3 | 2.63 | 0.013 |
| 200 | 0.08 | 0.21 | 11.2 | 3.55 | 0.034 |
| 215 | 0.04 | 0.24 | 10.7 | 3.30 | 0.032 |

| Depth, m | $Me_2Sb$ | Sb (III) | Sb (V) | MeGe * | $Me_2Ge$ * |
|---|---|---|---|---|---|
| 10 | <0.006 | 0.008 | 0.56 | 78.4 | 54.5 |
| 40 | <0.006 | 0.002 | 0.50 | 79.6 | 39.6 |
| 100 | <0.006 | 0.003 | 0.31 | 94.3 | 54.6 |
| 150 | <0.006 | 0.004 | 0.20 | 114 | 67.8 |
| 175 | <0.006 | 0.008 | 0.25 | 88.2 | 54.3 |
| 200 | <0.006 | 0.150 | 0.18 | 83.3 | 53.4 |
| 215 | <0.006 | 0.137 | 0.18 | 108 | 75.3 |

*In pmol litre$^{-1}$.

The dominant dissolved forms of other important TE in certain oxidation states cannot be determined in NW with the aid of the analytical methods employed. They include Pb(II), Mn(II), Co(II), Ni(II), Fe(III), and Sn(IV).

Organoelemental compounds have now been found in NW only for Group IV and V and also mercury owing to the hydrolytic and oxidative instability of the element-carbon bonds for other TE. With rare exceptions, only the methyl derivatives of TE have been detected in NW, although thousands of tonnes of ethyl, butyl, and phenyl compounds of the most toxic TE (Hg, Pb, As, and Sn), some of which ultimately enter the NW, are produced annually by the chemical industry. However, these compounds are unstable and decompose in NW as a consequence of microbiological and chemical processes accompanied by the subsequent natural methylation with formation of methyl derivatives of TE (see Section VII).

The methyl compounds of As and Sn were examined above. Among the methylmercury derivatives, MeHg(II) has been found in the coastal sea waters of Japan at a concentration of 0.1 ng litre$^{-1}$ [81] and in the river waters of Japan and Canada at concentrations in the range 2–8 ng litre$^{-1}$,[93] which amounts to 1 and 30% respectively of the total content of mercury in these waters. In addition $Me_2Hg$ at concentrations of 0–4 ng litre$^{-1}$ has been detected in the surface waters of Japan.[153]

More detailed data have been compiled for Group IV elements. The methyl compounds of germanium have been found in the Sargasso and Bering Seas and also in the

river and estuary waters of the USA and Portugal at concentrations in the following ranges (ng litre$^{-1}$): Ge(IV)—0.4–12.3 and 0.6–7.4, MeGe(IV)—18.2–24.5 and 0–19.6, $Me_2Ge$(IV)—8–11.5 and 0–12, and $Me_3Ge$(IV)—0 and traces.[32] The vertical profiles for MeGe(IV) and $Me_2Ge$(IV) in the Baltic Sea are presented in Table 5.

The concentrations of methyltin derivatives in the rivers of the USA and Europe are indicated in Table 6. Only 5% of the total tin exists in the methyl form[154] but its content in the form of these compounds increases sharply in the polluted rivers of Florida (up to 54%)[33] and in the Rhine (up to 94%).[154] The following amounts of different tin derivatives have been found in the coastal waters and surface waters mainly in the USA and Canada (ng litre$^{-1}$): MeSn(IV)—0–42[33,155,156] and 0–1220,[33,52,56] $Me_2Sn$(IV)—0–200[33,155–157] and 0–400,[33,52,156] $Me_3Sn$(IV)—0–400[33,157] and 0–50,[33,52] and $Me_4Sn$—480 and 930.[157]

Table 6. The content of the chemical forms of tin (pmol litre$^{-1}$) in certain rivers of the USA and Europe.[154]

| River | MeSn (IV) | $Me_2Sn$(IV) | $Me_3Sn$(IV) | Sn(inorg.) | Sn (total) |
|---|---|---|---|---|---|
| Colorado | traces | 1.7 | 1.7 | 21.1 | 24.5 |
| Mississippi | 11.8 | 26.1 | 0.8 | 1036 | 1075 |
| Ochlockonee | 1.7 | 0.8 | 0.8 | 35.4 | 38.7 |
| Rhine | 592.3 | 1769 | 13.5 | 155 | 2530 |
| Main | — | 3.4 | 2.5 | 101.1 | 107 |

Large concentrations of butyl derivatives of tin have been detected in Lake Michigan and in the surface waters of Canada (ng litre$^{-1}$): BuSn(IV)—56–8480; $Bu_2Sn$(IV)—10–7300,[52,156] and $Bu_3Sn$(IV)—10–2910. The content of the last form in the rivers and lakes of Switzerland is only 1–15 ng litre$^{-1}$.[158] It is believed that these butyl compounds are of anthropogenic origin and enter NW as a result of, for example, leaching from the paint on boats and ships or as a result of transport through the atmosphere.[52] A difference has been discovered in the interaction of various forms of tin with inorganic and organic substances in NW.[159] The stability and degree of decomposition of organotin and organolead compounds under natural conditions in aqueous systems depend greatly on the number of organic groups linked to the metal.[160,161] Silicones at concentrations ranging from 2.0 to 54.2 μg litre$^{-1}$ have been detected in the rivers of Japan.[162]

## V. COLLOIDAL AND SUSPENDED PARTICLES

### 1. Composition, Properties, and Distribution of Particles

It has come to be assumed that filtration of samples of NW through membrane filters with a pore size of ~0.45 μm makes it possible to separate the suspended forms of any chemical ingredients from the dissolved forms. However, it has been frequently found that the dissolved forms usually contain fairly numerous submicron particles and organic macromolecules (see, for example, Refs.10, 163, 164), which are colloidal particles in terms of their size and whose origin, composition, and nature have so far been little investigated. It has been shown that the composition and content of 0.0012–0.4 μm colloidal particles isolated from river and estuary waters depend on the time of year and the salinity.[165] During the winter, fresh water colloids, which consist mainly of the products of continental erosion (argillaceous minerals and iron oxide), become enriched in carbon with increase of the salinity of water and their content falls sharply from 28.6 to 0.6 mg litre$^{-1}$. During the summer, these colloids are enriched mainly in carbon of biogenic origin and their concentration changes insignificantly, from 1.9 to 0.7 mg litre$^{-1}$, with increase of the salinity of water. According to data obtained by the pyrolysis of the organic fraction of these colloids, it is suggested that it consists mainly of the secretions and decomposition products of the phytoplankton and micro-organisms.[166] It has been shown[167] that the average content of colloidal carbon in coastal sea waters is 0.15 mg litre$^{-1}$ regardless of the season, which corresponds to 11% of the total non-suspended carbon. It has been found that Fe(III) in river waters is present in the form of colloids stabilised by organic matter,[163,164,168,169] detergents, silicates, and phosphates, but not chlorides, nitrates, hydrogen carbonates, and sulphates.[169] The main bulk of colloidal Al is also coated by organic matter; the degree of adsorption of TE by these colloids depends on the stability of the complexes formed by the TE with organic ligands.[170]

The colloids in fresh water consist of electrically charged particles, whose charge is due to the presence of unsaturated and ruptured bonds on the surface of the crystal and the substitution of structural cations in the mineral lattice by cations in another valence state. The charge on the surfaces of inorganic colloids can be both positive (Al hydroxides at a high pH) and negative (quartz or argillaceous minerals), while in organic colloids (HS) it can only be negative. The negative charge of the colloids is balanced by binding the TE as a result of ion exchange, surface adsorption, and chelation.[99,171]

The content of the suspension in river waters varies from a fraction of a milligram to tens of grams per litre. Its average concentration in world rivers is ~0.5 g litre$^{-1}$ and the maximum and minimum concentrations in the rivers of Asia and South America are 1.28 and 0.095 g litre$^{-1}$ respectively.[172] In the waters of the open ocean its content is lower by several orders of magnitude: depending on the season, it changes by up to several hundreds of micrograms per litre in surface waters and is on average 10 μg litre$^{-1}$ at depths in excess of 200 m.[173] The main bulk of the suspended particles have dimensions less than 10 μm in both river[94] and sea[173] waters, but the size of the biological particles formed in the ocean can reach 1 mm.[173]

The river suspension contains an amount of organic matter ranging from several tenths to 20%[172,174] while in ocean water it is 30–70%.[173] Quartz and argillaceous minerals (illite, chlorite, montmorillonite, and kaolinite) predominate in the terrigenous (mineral) river suspension,[172] while aluminosilicate particles, incorporating clay and non-aqueous minerals and also non-aluminosilicate minerals (quartz, pyrite, dolomite, barite, titanite, and iron and titanium oxides) predominate in coastal sea water.[175]

The main bulk of the suspension in surface ocean waters is of biological origin, consisting of carbonates, opal, and cellular and amorphous organic matter.[173,176] Its fraction is 60–90% of the total amount of the suspension entering deep waters down to 5000 m[177–180] (for example, the suspension collected in deep water traps contained 0–25% of clay, 60–70% of $CaCO_3$, 0–15% of opal, and 8–12% of organic carbon[180,181]), despite the fact that most of the suspension is mineralised and is consumed by hydrobionts following submersion.

The terrigenous component of the entire oceanic suspension is only 0.5–10%,[176] but, in contrast to the biogenic suspension, it does not dissolve and does not change in the bulk of the water and in sediments in water. A suspension of anthropogenic origin has been found in deep waters.[182]

It follows from data for the basic chemical composition of the suspensions in many world rivers[94,172] and also from the average compositions[172,183] that river suspensions occupy, in terms of their composition, an intermediate position between sedimentary rocks and soils. This indicates the source from which they originate. The basic chemical composition of a marine suspension has also been investigated.[184,185]

## 2. The Overall Content and Distribution of TE

Table 7 presents the content of certain TE in suspensions in the major world rivers. Among individual countries, this question has been most fully investigated in Japan, where 21 suspended TE have been determined in each of 166 rivers.[187] The highest concentrations in the suspension are usually those of Fe and Mn and in the Mississippi, for example, their contents reach 46.1 and 1.3 mg $g^{-1}$ respectively.[87]

Table 7. The contents of TE in suspension in certain world rivers (μg $g^{-1}$).

| River | Co | Cr | Cu | Ni | Pb | V | Zn | Refs. |
|---|---|---|---|---|---|---|---|---|
| Amazon | 41 | 193 | 266 | 105 | 105 | 232 | 426 | [183] |
| Congo | 25 | 175 | — | 74 | 455 | 163 | 400 | [183] |
| Ganges | 14 | 71 | 30 | 80 | — | — | 163 | [183] |
| Garonne | 39 | 255 | 51 | 33 | 381 | 150 | 874 | [183] |
| Mekong | 20 | 102 | 107 | 99 | 113 | 175 | 300 | [183] |
| Mississippi | 21 | 72 | 42 | 55 | 45 | — | 184 | [183] |
| Niger | 40 | 150 | 60 | — | — | 180 | — | [183] |
| Yangtze Kiang | 25 | 83 | 70 | 78 | 65 | — | 108 | [186] |
| Yellow River | 12 | 72 | 33 | 38 | 35 | — | 75 | [186] |
| Danube | 16 | 140 | 189 | 89 | — | — | 322 | [172] |
| Dnieper | 5 | 86 | 90 | 93 | — | 90 | 260 | [172] |
| Don | 12 | 143 | 200 | — | — | — | 870 | [172] |
| Volga | 11 | 183 | 86 | 76 | - | 102 | 260 | [172] |

The contents of the suspended forms of TE in surface waters depend on the concentration of the suspension, its mineralogical and granulometric compositions, the climatic zone, and the time of year. Thus the concentrations of the suspended TE in various sections of the river proved to be inversely proportional to the content of the suspension in those sections,[188] while in Lake Ontario they were found to depend on the distance from the shore and amount on average to 50–80, 10–40, 20–60, and >60% of the overall concentrations of Cu, Ni, Cd, and Pb respectively.[189]

The contents of the suspended Hg and MeHg(II), which predominate during spring flooding, fall sharply during the summer period.[190]

It is impossible to say *a priori* which of the principal various forms of the TE, suspended or dissolved, is the main one in river waters. Al, whose suspended form always predominates, is an exception.[86,172,183] It has been shown that Fe and Mn,[86] Fe,[191,192] Fe, Mn, Ni, Co, Cr, and Pb,[183] and Cd, Pb, and Cu[193] predominate in the river suspensions; there is more than 90% of the Fe, Mn, Cd, Cr, Cu, Ni, Pb, and Zn in the suspension from the Mississippi[87] and more than 98% of the Hg from the Thames.[92] The relative importance of the suspended forms diminishes in the sequence Al > Fe > Mn > Co > Zn > Ni > Cu > Cd.[86] On the other hand, the dissolved form predominates for Ni, Cu, Zn, and Cd[86] and for Mn;[193,194] ~70% of Mn, Cu, and Zn and 100% of Cd[191] and more than 75% of Fe, Cd, Cu, and Zn[195] exist in this form. In order to arrive at correct conclusions from geochemical studies, it is desirable to carry out monthly measurements of the concentrations of these forms of TE in rivers over a period of many years.[86] Nevertheless one should note that the vast majority of TE are transported in rivers mainly in the suspended form.[88,172,183]

As a consequence of the low concentrations of the suspension in sea water and particularly ocean waters, they contain much smaller amounts of suspended TE than river waters. For example, the concentrations in the waters of the Central Atlantic are as follows (ng $litre^{-1}$): Al—78, Mn—3.5, Fe—222, Cr—3.1, Ni—1.8, Cu—3.6, Pb—4.5, and Zn—16;[22] the concentrations found in the Southern Indian Ocean are (in ng $litre^{-1}$ and μg $g^{-1}$ respectively) Pb—35 and 260, Cd—3.5 and 26, Cu—100 and 730, and Zn—230 and 1700.[196] The suspended TE have also been determined in the waters of the Baltic Sea,[184] the Alaska Bay,[185,197] and in the plankton of the Pacific Ocean.[198] Turning now to individual TE, we may note that the concentrations of suspended mercury are (ng $litre^{-1}$) 0.2–0.3 in the coastal waters of Japan[94] and 0.5–0.9 in the Pacific Ocean and the Sea of Okhotsk[63] and those of suspended Cr are 80 in the Sea of Japan and 70 in the Pacific Ocean.[85] Pressure can exert a considerable influence on the interaction of the dissolved Al with the inorganic detritus in the bulk water, the bottom deposits, and at the water–deposit interface.[199] The importance of adsorption on the submerging organic suspension for the rapid decrease of the concentration of Hg in coastal sea waters has been emphasised.[122]

The proportions of the suspended forms of TE relative to their total content may be as follows: 3–10 for Hg,[63] 10–30 for Ag (Pacific Ocean),[61] and 1.7, 3.3, and 9.8% respectively for Zn, Cd, and Cu (Baltic Sea).[200]

The majority of the dissolved TE are finally removed into the deposit in the seas and oceans by becoming adsorbed on suspended particles. Biogenic particles formed initially in the surface layer from the phytoplankton and ultimately submerged into deep regions in the oceans in the form of detritus (the main bulk of which consists of fecal pellets whose rate of submersion ranges from several to thousands of metres per day) play an especially important role in controlling the distribution of TE in oceans.[1] A different fraction of each TE in the suspension is remineralised and passes to the bulk water, while another fraction of TE is found in pelagic clays and iron–manganese concretions and is then returned to surface waters by upwelling.

The rates of scavenging, which is an important factor limiting the concentrations of certain TE in oceans, and of the removal of TE from deep waters into deposits have been found.[181,201–203] For example, the rates are 20–50 μmol $cm^{-2}$ $g^{-1}$ for Mn and Fe and 0.1–0.4 μmol $cm^{-2}$ $g^{-1}$ for Cu, Co, Ni, Zn, V, and Sr.[203] The fluxes of suspended TE directed towards deep waters can undergo seasonal variations connected with the cyclic nature of the primary production,[202]

biogenic particles binding TE more strongly than mineral particles.[204]

### 3. Physicochemical Forms of TE

In a suspension TE can exist in stationary forms (the crystal lattice of undecomposed fragmented and argillaceous minerals) and mobile forms (surface sorption on organic matter and Fe and Mn hydroxides), only the latter being biologically accessible. It is noteworthy that there are at present no methods for the independent determination of the individual physicochemical forms of TE in a suspension, which seriously hinders comparison of the results obtained by different workers.[172, 205, 206]

The crystalline form and Fe and Mn hydroxides are usually most important in river suspensions.[172] For example, in the Amazon and Yukon rivers these forms comprise together 65–92% of Fe, Mn, Co, Cr, and Cu.[88] The predominance of both mobile[172,207] and organic and Mn hydroxides[207] forms has been noted for a series of TE. Differences between the ratios of different forms of TE in different granulometric fractions of the suspension have also been discovered.[207, 208]

In conformity with the significant difference between the compositions of river and marine suspensions noted above, it has been shown[209] that up to 70% of Al, Mn, Zn, Cu, Pb, and Li in the suspensions in the Indian Ocean exist in the adsorbed form and the form bound to Fe and Mn hydroxides and only 15% of these TE exist in the organic form, while in the inner seas the latter form reaches 30–70%, which is apparently associated with the vigorous absorption of the TE by the phytoplankton.

### 4. The Mechanisms of the Binding of TE

The suspended particles and deposits in aqueous media concentrate TE via three main mechanisms:[206] via their physicochemical adsorption from the bulk of the water, via their biological absorption, and via the sedimentation of the TE-enriched suspension. The degree of physicochemical adsorption, subdivided into physical and chemical, and also ion exchange[210] are influenced by the nature of the surface of the suspension or of the deposit in the aqueous medium.

The physicochemical adsorption of TE in different types of NW on the surfaces of clay, solid organic substances, and metal oxides is of greatest importance. Although previously very much more attention was devoted to the sorption of TE by clays, it is believed nowadays[206] that, in the adsorption of TE from NW, clays probably play the role of supports covered by organic matter or metal oxides. The surface of the clay will therefore not be considered here.

There exist three types of organic surfaces:[206] (1) the surfaces of living organisms such as bacteria and algae and, which is particularly important, the surface of marine plankton in which the main bulk of the TE are bound to non-skeletal organic phases and not to calcium carbonate and opal;[198] (2) the surface arising on decomposition of plant and animal matter and also on condensation of low-molecular-weight organic substances to form high-molecular-weight organic substances; it possesses many of the properties of polyelectrolytes and colloidal particles; (3) the surface formed by low-molecular-weight organic substances sorbed on clay or metal oxide supports.[211, 212]

Although the differences between these three types of organic surfaces have not been ultimately elucidated from the standpoint of the method of concentration of the TE by the latter, it has come to be assumed that salicylic acid is involved in the binding. The participation of carboxylic and phenolic functional groups[212,213] and also peptides[214] in the mechanism of the binding of TE has also been suggested.

We may note that the models of the reactions taking place on the surface in the absence of organic matter cannot be applied to natural systems, because in this case organic matter is adsorbed on the surface of the suspension,[213, 215] which is at least partly responsible for the negative electrostatic charge on almost all suspended particles.[211, 216] The amount of adsorbed organic matter then depends on the chemical composition of the surface of the suspension.[215]

Hydroxy-groups are present in water on the surfaces of metal oxides, the most important of which are $Al_2O_3$, FeOOH, and $MnO_2$.[4] The specific adsorption of cations and anions is therefore regarded as a result of their interaction with these groups at the water–oxide interface. The degree of binding of TE ions on the surface depends on the concentration of the reacting groups and the competing ions and also on the pH and the ionic strength of the medium.[206] Several mechanisms have been proposed to explain the sorption of TE,[217] including ion exchange, surface ionisation, and complex formation—in particular the formation of Zn and Pb phosphates.[218]

The picture becomes still more complex where one considers heterogeneous oxide surfaces, where the strengths of the bonds between TE and various centres can differ by an order of magnitude.[219] Hydrated oxide surfaces can adsorb organic matter also via ligand exchange. The degree of adsorption then depends on the pH and the MW.[206]

It must be emphasised that natural organic matter binding TE can be present in NW both in the dissolved state and in the form of a thin film coating the suspended particles. Natural organic matter can be regarded as the most important factor in the TE cycle in NW.[201, 205] This has been demonstrated for the waters of the open ocean where the distribution of the majority of TE is controlled by their biological absorption on the surface and their regeneration in deep waters from submerged biogenic residues.[1]

## VI. ESTUARINE MIXING

Estuaries, which may be any water area where sea water mixes with the fresh water from the continental slope, namely river mouths, coastal bays, marshes, and basins behind a coastal bar constitute at the same time zones where there is a transition from the continent to the ocean and the continuity of the properties of the environment breaks down. A wide variety of hydrodynamic, physicochemical, and biological processes take place in estuaries at the geochemical river–sea barrier.

As a result of the sharp decrease of the flow rate of the river, estuarine mixing entails the deposition of more than 90% of the river suspension together with the TE bound to it.[172,220–223] Small particles whose size is less than 2–5 μm can be removed from the bulk of the water also as a result of the increase in their size as a consequence of coagulation, which arises on neutralisation or charge transfer involving clay particles, caused by the mixing of river waters with sea water, which is a strong electrolyte.

The concentrations of the inorganic and organic substances present in the suspended, colloidal, and dissolved states change sometimes very considerably, not only as a result of the mutual dilution of the fresh and sea waters but also as a consequence of various physicochemical transformations occurring under the non-steady conditions of the estuarine environment owing to the sharp changes over small distances

in salinity, pH, the content of the suspension, and other factors. Such transformations include precipitation, sorption, flocculation, complex formation, and other processes. The 2% isohaline is regarded as the hydrochemical boundary between the river and sea waters,[172] although the relative contents of the principal ions are almost constant only after 10% has been reached.

The causes of the observed variations in the content of both suspended and dissolved principal and trace elements in estuarine waters are not, however, altogether clear owing to the lack of complete hydrochemical and hydrodynamic information.[220,224] Sorption processes are frequently invoked to account for these causes. It has been shown that, among the principal cations, the Ca in the suspension exchanges for Na and to a lesser extent for K, while Mg is little involved in exchange reactions.[225] Among the TE, Fe,[226] Mn,[224,227] Cu,[224,228] Cd,[227,229] Pb,[120] and Ba, Co, Cs, and Zn[229] are desorbed into water. The increase in the concentrations of the dissolved TE, for example, Cu, is frequently attributed to their mobilisation from the resuspended deposits in aqueous media at high salinities[228] (for further details, see Section VII).

Overall, a clear idea about the role of sorption in estuarine processes is lacking. On the other hand, there is important evidence for the predominance of the influence of physical[224,230,231] (for example sedimentation and hydrological[230]) processes, and not physicochemical processes, on the chemical composition of the suspension in estuaries.

In the estuarine mixing of waters, the suspended or dissolved components behave conservatively when they participate only in a physical (mechanical) mixing process or non-conservatively when they are involved in various physicochemical reactions or in biological turnover. In the former case their concentrations depend linearly on the salinity and the input or removal of the components can therefore be estimated from the observed deviations from the straight line.[220]

An extremely important process for dissolved inorganic and organic substances in the estuary zone is their flocculation, i.e. their transformation into suspended amorphous particles, which takes place with increase of the salinity and pH of the water. The most important precondition for flocculation is the presence in river waters of dissolved Fe, which is believed, on the basis of a series of indirect data, to exist mainly in the form of Fe(III) hydroxides stabilised in the colloidal state by chemical binding to HA[99,163,168] (although recently objections have been raised against the latter hypothesis[232]). In the estuarine mixing of waters, the colloidal Fe and HA flocculate as a consequence of their destabilisation by cations from sea water.[163,168] However, it is not altogether clear whether this destabilisation of river colloids is associated with complete[163] or only partial[233] neutralisation of the negative charge. In contrast to Fe and HA, dissolved organic matter behaves conservatively.[164,168,233–235] The rate of flocculation increases with increasing salinity up to 15–18% and, for certain salinities, the bulk of the floccules are formed in the first 0.5 h after the start of mixing.[236,237]

Flocculation is the principal mechanism of the removal of dissolved TE from river water via coprecipitation and adsorption on the Fe hydroxide and HA floccules formed.[236,237] For example, TE can be removed from river water to the following extent:[236] 95% for Fe, 20% for Al, 40% for Cu and Ni, 25–45% for Mn, and 10% for Co. As[142] and Hg, Bi, and Sn[229] also flocculate. We may note that 65% of their HA is then lost, which, however, corresponds to only 3% of the dissolved organic matter.[168] The content of organic matter in river waters can be a regulating factor in the removal of TE;[238] the lanthanide elements are removed to the extent of 60–95% at a high concentration of organic matter and remain in the water at a low concentration. The removal of TE in the estuarine zone has been the subject of field observations.[115,163,172,224,239,240] The degree of removal can depend significantly on the form of the TE. For example, the inorganic colloidal form of Fe is removed quantitatively, while the organic form is removed only to the extent of 50%.[119] Estuaries behave as traps for TE in the course of their transfer from river to sea water, which may serve as one of the explanations of the relatively low concentrations of TE in the marine environment compared with the river environment.[241]. At the same time the conservative behaviour of Mn,[164,172,235] Cu,[115,242,243] Ni,[242,243] Cd and Zn,[242] and Cr[244] has been demonstrated. The form of the TE can strongly influence its behaviour: for example, compounds having the composition $R_nPb$ (where R is an organic group) behave conservatively, while inorganic Pb behaves in the opposite manner.[245]

Overall, the geochemistry of the TE in estuaries, which depends also on their type and the physicogeographical conditions in the environment, is very complex and so far has been little investigated. The ideas concerning the behaviour and estimation of the losses of dissolved and suspended TE in various river estuaries are frequently contradictory and vary markedly. The atmospheric input of TE also has an effect.[246] Nevertheless it can be regarded as demonstrated that estuaries serve as traps for the majority of the dissolved and suspended substances on their way to the ocean.

## VII. BOTTOM DEPOSITS AND PORE WATERS

### 1. Total Content and Distribution of TE

Marine, coastal, and estuarine deposits usually consist of two layers—the upper oxidised reddish-brown layer and the lower reduced olive-green layer. Variations in the thickness of the oxidised layer up to 1 mm depend on the input of organic matter on the bottom and on the rates of its decomposition (destruction). Oxygen diffuses downwards through the oxidised layer and the free $H_2S$, formed in the reduced layer by sulphate-reducing bacteria, diffuses upwards (sometimes without being evolved[247]). The reduced layer contains benthic organisms. It has been shown recently[248] that the colour transition from brown to green in marine deposits is accompanied by the reduction of Fe(III) to Fe(II) in pore waters.

In water areas with limited circulation, for example in the Black Sea and in fjords, oxygen does not reach deep waters and for this reason $H_2S$ is present even near the bottom layer. In this case the deposits are coloured black and contain no benthic organisms.

The pore waters impregnating the bottom deposits always differ in their chemical composition from the water covering them (bottom water) by the fact that their concentrations of dissolved $O_2$ and $SO_4^{2-}$ are reduced and those of bicarbonate are increased. Not only $SO_4^{2-}$ may be reduced to $H_2S$ but also $CO_2$ and $NO_3^-$ may be reduced to $CH_4$ and $NH_3$ respectively in the pore waters of the reduced deposits.

As a consequence of the occurrence of diagenetic processes in ageing deposits, mainly in the pore waters, the chemical composition of the latter is important for the elucidation of the mechanism of the diagenesis. However, despite the fact that pore waters are usually enriched in the TE by a factor of 10 and more compared with the main bulk of the water, the contribution to the overall TE content in the wet deposit is insignificant (for the bibliography, see Warren[249]).

The bottom deposits are enriched in TE mainly as a result of three processes: (1) the sinking to the bottom of suspended particles; (2) the transfer of suspended particles along the bottom (in rivers); (3) the sorption of dissolved TE from water when the latter comes into contact with a deposit. The most important process is the sedimentation of the suspension in which one can isolate the detritus, biogenic, and deposited fractions. The particles of detritus contain TE within crystal lattices, in the adsorbed state on the surface, in the exchange centres of argillaceous minerals, and in surface layers formed by metal hydroxides or organic matter. Biogenic particles can contain TE within skeletal inorganic substances, in the adsorbed state on the surfaces, in exchange centres, in organic matter, in a bound form, and in the envelopes coating metal hydroxides. In the deposited fraction, which includes calcium carbonates and metal hydroxides and sulphides, the adsorbed TE are present on the surface.[249]

The content of TE in deposits from different water areas varies markedly, sometimes by 2–3 orders of magnitude, mainly in connection with the different degrees of their contamination. The concentration of TE in coastal,[250] lake and sea[249] deposits have been considered in a number of reviews. The contents of cadmium in deposits of different types have been analysed.[251] There exist data on the concentration of TE in river,[252,253] lake,[189,254] coastal,[197,255–264] and ocean[265] deposits.

The estuarine deposits, which behave as traps for the many suspended and dissolved TE carried out by the rivers, belong to the class of the most polluted. Their contents of some TE are listed in Table 8. The Rhine estuary and New Jersey river estuaries, whose deposits contain considerable concentrations of Pb and Cu, have attracted attention. The concentrations of As in the deposits in 27 estuaries in Great Britain differ by 3 orders of magnitude. In particular, its content in the Thames estuary is 4–6 μg $g^{-1}$,[274] while its maximum concentration reaches 2500 μg $g^{-1}$.

Table 8. The average TE concentrations in estuarine deposits (μg/g of dry mass)

| Estuary | Mn | Cu | Cd | Ni | Pb | Hg | Zn | Refs. |
|---|---|---|---|---|---|---|---|---|
| Ems | — | 24 | 0.7 | 27 | 47 | — | 150 | [266] |
| Rhine | — | 99 | 5.0 | 31 | 213 | — | 870 | [266] |
| Weser | — | 42 | 2.4 | 58 | 154 | — | 393 | [267] |
| St. Laurence | — | 24 | 0.22 | 33 | 30 | 0.45 | 115 | [268] |
| Miramichi | 417 | 27 | — | 45 | 83 | 0.34 | 219 | [269] |
| Ko-Jima | 703 | 37 | 0.61 | — | 27 | — | 177 | [270] |
| New Jersey rivers | — | 66 | 2.24 | 36 | 128 | 0.66 | 218 | [271] |
| Mersey | 564 | 41 | 5.3 | — | 57 | — | 236 | [272] |
| St. John | 296 | 16 | 0.16 | 16 | 24 | 0.04 | 53 | [273] |

The distribution of mercury has been studied in particular detail in European countries. Thus its content in the deposits in more than 30 estuaries in Great Britain is 0.018–29 μg $g^{-1}$,[275–279] while the deposits of 220 Swedish lakes contain 0.05–0.5 μg $g^{-1}$ of mercury[280] although sewage had never been previously discharged into the lakes investigated. The mercury content in oceanic deposits is correlated with the underwater volcanic activity.[281]

The TE which have entered various water areas in a wide variety of ways—from the atmosphere, from rivers, from sewage discharges, etc.—inevitably accumulate in the bottom deposits. The bore cores of bottom deposits removed without disturbing the stratification can therefore reflect the entry of TE into the water basins over any period of time, up to 100 years. The geochronology of bottom deposits is usually determined by analysing the distribution of the $^{210}Pb$ isotope with respect to depth, but, in order to achieve a more accurate dating, combinations of different isotopes are employed, their number being fairly considerable (for example, $^{137}Cs$, $^{238}Pu$, $^{239,240}Pu$, $^{241}Am$, and $^{244}Cm$).[282]

The TE concentrations in the surface layers of lake, estuary, and coastal sea deposits in the vicinity of mining, industrial, and city regions can be a factor of 5–10 higher than 50–100 years ago, which indicates their anthropogenic origin. Apart from the information contained in a study mentioned previously,[16] there exist data on the geochronology of TE in the bottom deposits in fords,[283] lakes,[282,284–288] rivers,[282,289] estuaries,[290,291] fjords,[292–294] and coastal sea regions.[295–298] The historical record in the vertical Zn, Pb, Cr, Cu, As, Ni, Cd, and Hg profiles in the Rhine deposits over a period greater than 50 years is illustrated in Fig. 2.[289]

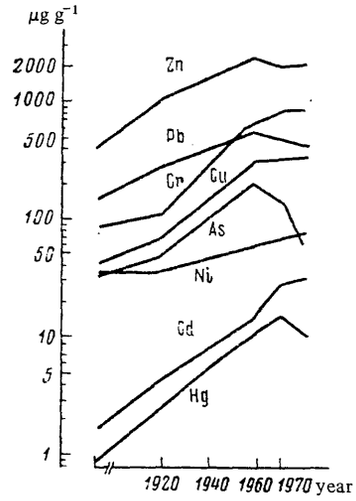



Figure 2. Time variation of the concentration of TE in the bottom deposits of the River Rhine.[289]

However, TE are distributed non-uniformly in deposits and their concentrations usually increase with decreased particle size.[249] The difference between the concentrations reaches in some cases an order of magnitude and more. The observed scatter can be appreciably reduced by employing different correction procedures.[15,299] A fraction whose size is less than 63 μm is usually analysed,[300] although it has been shown[299] that the content of many TE in a fraction up to 20 μm in size from estuarine deposits varies several times less from sample to sample than for a fraction whose size is up to 63 μm. Systematic investigation of different types of bottom deposits is therefore essential for a final selection of the fraction size most suitable for the monitoring of TE.

## 2. The Physicochemical and Chemical Forms of TE

The TE within bottom deposits are distributed between various physicochemical forms (geochemical fractions), which depend on Eh and pH[301] and differ in their mobility, leachability, and biological accessibility. In order to make it easier to understand the geochemical distribution of TE, the deposits are usually fractionated geochemically by methods involving single- or multi-stage consecutive extraction, which make it possible to leach selectively, with the aid of suitable chemical reagents, each of the identified fractions. The TE linked to the crystal lattice of silicate rocks are referred to as lithogenic and the corresponding fractions are called residual. The TE present in all the remaining geochemical fractions are referred to as non-lithogenic and the degree of pollution of the given deposit (water area) can be inferred from the level of their concentrations.

The single-stage extractions (they have been assessed and compared in a number of studies[302–304]) make it possible to determine either some one of the non-lithogenic TE fractions or their various combinations depending on the pH[305] and the reagent employed. In order to investigate more fully the physicochemical forms of TE, extractions comprising two,[289] three,[306] four,[272] five,[267, 303, 307] six,[308] and seven[15] steps are used. The advantages and disadvantages of the extraction methods have been discussed.[15, 302, 309, 310] It must be emphasised that the multistage consecutive extraction methods are not fully selective, the reactions being always influenced by factors such as, for example, the extraction time, temperature, the ratio of the volumes of the deposit and the extractant,[15, 309] and the readsorption of the TE.[311] Despite this, they are used widely.

Depending on the origin, composition, and degree of pollution of the deposit, the main bulk of the TE may be located in different geochemical fractions. The non-lithogenic TE are frequently bound to organic matter,[205, 269, 272, 308, 312, 313] which is particularly characteristic of mercury,[259, 275, 277, 278, 314] and also to the oxides of Fe (the main bulk of As[315–317]) and Mn,[205, 259, 308, 317–320] sulphides,[259, 313, 320] carbonates,[320–322] and phosphates.[319] Oceanic deposits have also been investigated.[317, 323]

Table 9. The physicochemical forms of TE (%) in the bottom deposits of the Rhine (A) and the Ems estuary (B).[15]

| Forms | Zn | | Ni | | Cu | | Pb | | Cd |
|---|---|---|---|---|---|---|---|---|---|
| | A | B | A | B | A | B | A | B | A |
| Exchangeable | 9 | 2 | 6 | 3 | 1 | 2 | 3 | <1 | 18 |
| Carbonate | 37 | 31 | 13 | 10 | 28 | 19 | 52 | 35 | 38 |
| Readily reducible | 39 | 24 | 25 | 28 | 3 | 3 | 6 | 4 | 23 |
| Moderately reducible | 5 | 12 | 17 | 15 | 30 | 29 | 23 | 29 | 1 |
| Non-silicate iron | 1 | 2 | 6 | — | 2 | 5 | 6 | 11 | — |
| Organic and sulphide | <1 | 3 | 3 | 6 | 4 | 3 | <1 | <1 | 6 |
| Residual | 9 | 26 | 40 | 38 | 32 | 39 | 10 | 20 | 14 |
| Total concentration, μg g$^{-1}$ | 922 | 227 | 84 | 42 | 209 | 26 | 144 | 66 | 10 |

Examples of the application of the seven-stage extraction to deposits from the Rhine and from the Ems estuary are presented in Table 9,[15] whose data indicate an appreciable decrease of the proportion of the residual fraction for Zn, Cu, and Pb, despite the increase of their overall concentration, as a consequence of the pollution of the deposit. Appreciable amounts of Zn, Cu, Cd, and Pb are present in the carbonate fraction, while the proportion of the exchangeable form is appreciable only for cadmium.

With the exception of mercury, the chemical forms of TE have been little investigated in deposits. It has been shown that the MeHg(II) content in various estuarine and coastal deposits is usually less than 1% of the total Hg.[275, 278, 324] The MeHg(II) concentration is largely controlled by the content of sulphides and not of the total Hg and organic matter. At a specific concentration of sulphides, the level of MeHg(II) falls sharply, apparently as a consequence of a disproportionation reaction:

$$2\mathrm{MeHg(II)} + S^{2-} \rightarrow (Me_2Hg)_2S \rightarrow HgS + Me_2Hg.$$

The dimethylmercury formed vaporises and is transferred through the bulk water to the atmosphere.[279]

The predominance of a particular form of tin depends on the type of deposit.[155] In partly reduced and polluted marine deposits MeSn(IV) predominates, in oxidised and polluted deposits the main component is $Me_2Sn(IV)$, while in oxidised and unpolluted deposits $Me_3Sn(IV)$ is the main component. It has been shown[155] that the deposits from the Baltic and Mediterranean Seas contain 0.5 and 0 ng g$^{-1}$ of the first form respectively, 0.3 and 2.6 ng g$^{-1}$ of the second form respectively, and 0 and 8.6 ng g$^{-1}$ of the third form respectively. The following butyltin derivatives have been detected in deposits from Canadian lakes (μg g$^{-1}$):[325] $BuSn(IV)$—0.013–0.58, $Bu_2Sn(IV)$—0.05–0.35, and $Bu_3Sn(IV)$—0.11–0.40. Mixed compounds, formed apparently as a result of methylation, have also been found: $Bu_2SnMe_3$—0.011–0.012 μg g$^{-1}$ and $Bu_3SnMe$—0.011–0.023 μg g$^{-1}$. The deposits from Swiss lakes contain 0.002–0.016 μg g$^{-1}$ of $Bu_3Sn(IV)$.[158] The river and coastal deposits were found to contain respectively 0.3–5.8 μg g$^{-1}$ [162, 326] and 0.61 μg g$^{-1}$ [326] of silicones.

## 3. Pore Waters

The concentration and distribution of TE and of their different forms in pore waters depend on Eh, pH, and the content and forms of organic matter and Fe and Mn compounds (amphoteric oxides, sulphides, carbonates, etc.). Pore waters constitute a medium in which TE are transported within surface deposits. The upper layer of these deposits 10–20 cm thick is most important for the exchange between deposits and the water near the bottom.[327] In marine deposits in the oxidised zone the concentrations of Mn and Ni are the same as in the water near the bottom, while in the Mn-reduced zone they are higher approximately by factors of 10 000 and 40 respectively.[328] The Cu content in oxidised pore waters is higher by a factor of 10 and more than in the water near the bottom.[328–330] This is due to the binding of copper by organic matter,[328, 330] which is also the cause of the increase in the Mo, V, and Cr concentrations in the reduced deposits with increase of depth.[331]

The pore waters in polluted deposits contain a particularly large amount of TE. For example, it was found that the pore waters in a lake contain approximately 0.15 mg litre$^{-1}$ each of As(III) and As(V),[332] river pore waters were found to contain 5.85–6.88 g litre$^{-1}$ of total As [including 6–10% of inorganic As and ~90% of $MeAsO(OH)_2$],[333] and the estuarine pore waters were found to contain 3.8 μg litre$^{-1}$ of Hg.[334] In the last case an increase of the Cr, Cu, Zn, Pb, Ag, Ni, and Fe concentrations by a factor of 7.3–15 and of the Mn and Co concentrations by factors of 620 and

37 respectively compared with the water near the bottom was noted.[335] Large seasonal variations have been observed in the Fe, Mn, Cu and Mo contents.[336] The Fe, Cr, and Cu concentration profiles in the bottom water and in the pore waters of coastal marine deposits are presented in Fig.3.[322]

## 4. The Remobilisation of TE

Under the influence of chemical changes in NW and microbiological processes in aqueous media, the TE present in bottom deposits can be remobilised and returned to the water. The remobilisation is induced by four types of chemical changes in water:[15] (1) by an increase of the concentrations of salts whose alkaline earth metal cations can compete with TE ions for sorption on particles; (2) by a change in the oxidation–reduction conditions, usually in connection with the decrease of the oxygen content as a consequence of increased eutrophication, whereupon Fe and Mn hydroxides dissolve, either partly or completely, owing to the reduction to Fe(II) and Mn(II) and some of the TE bound are then liberated (remobilisation of Mn, Cu, and Cd from partly reduced deposits with subsequent vertical transfer to the surface waters has been used to explain the increase in their concentrations in the shelf waters of Great Britain[337]); (3) by a decrease in pH, which leads to the dissolution of hydroxides and carbonates and also to an increase in the desorption of TE as a consequence of competition with $H^+$; it takes place either on oxidation of sulphides in uncontaminated surfactants or on precipitation of acid rain, which is characteristic of many lakes in Northern Europe and North America; in the latter case it has been shown[320] that Zn, Co, and Ni are remobilised mainly from the fraction of readily reducible deposits—Cd is remobilised from the organic phase, while Cu and Pb pass to water to only a slight extent; (4) by the increased employment of natural and synthetic complex forming agents, capable of forming soluble and stable complexes with TE, which would have otherwise been adsorbed on solid particles.

The biological remobilisation of TE can be achieved indirectly as a result of the activity of benthic organisms, which increase the ventilation of the deposits by the oxidised bottom waters[338, 339] and prevent thereby the formation of virtually insoluble sulphides of class B TE in pore waters.[340, 341]

The microbiological proesses in deposits where TE are bound to organic matter having a higher MW and a smaller number of functional groups as a result of diagenesis are more important. The remobilisation of TE takes place mainly in three principal ways:[15] (1) by the decomposition of the organic matter to compounds having a smaller MW but binding TE more effectively (see, for example, Graybeal and Heath[342]); (2) by the change in the physical properties of the medium, for example Eh and pH, as a consequence of metabolic activities; (3) by the conversion of inorganic TE compounds into organoelemental compounds.

## 5. Natural Methylation

Biomethylation is of greatest importance among the microbiological processes, since hitherto there has been no convincing proof of the biosynthesis of organoelemental compounds containing other alkyl or aromatic groups.[343] Apart from the experimental evidence for the biomethylation of TE in deposits described in reviews,[16,18,343,344] the biomethylation of As by fresh water green algae,[345] the methylation of Sn in estuary deposits,[157,346] and the methylation of Hg in the bulk of river,[347] lake,[348] and sea[349] waters have been observed recently. The seasonal variations in these processes[190,348] and the influence of sea salts on the formation and stability of MeHg(II) under aerobic and anaerobic conditions[350] and of the pH on the formation of methyl compounds of Hg and As[351] have been investigated.

The contents of the methyl derivatives of Hg, Sn, Pb, As, Sb, and Se in NW, in suspensions, and in deposits were indicated above in the appropriate Sections. In biological systems, in particular in micro-organisms, the methylating agents are Me–$CoB_{12}$, *S*-adenosylmethionine, and $N^5$-methyltetrahydrofolates. The mechanism of methylation by the $MeCOB_{12}$ reagent depends on the oxidation state of the TE and the reduction potential and can be electrophilic or radical.[18,343,352]

The biomethylation of TE is always accompanied by the reverse biodemethylation of their methyl derivatives,[16,344] which explains, in particular, the low concentrations of MeHg(II) in NW and deposits. The amount of mercury in this form is less than 1% of its total content.

However, one should note that by no means all biotransformations of TE have been elucidated. Thus, despite previous experimental data, the absence of the biomethylation of Pb[353] and $Me_3SnCl$[354] has been demonstrated recently. The compounds $Me_4E$ (E = Sn or Pb), formed as a result of chemical disproportionation, for example, in the presence of sulphur compounds, have been detected:[354,355]

$$2Me_3E(IV) \xrightarrow{S^{2-}} (Me_3E)_2S \rightarrow Me_4E.$$

In river deposits HA and fulvoacids can also methylate Hg(II) to MeHg,[103,356] and, among the methylating agents forming part of their composition, the most powerful is

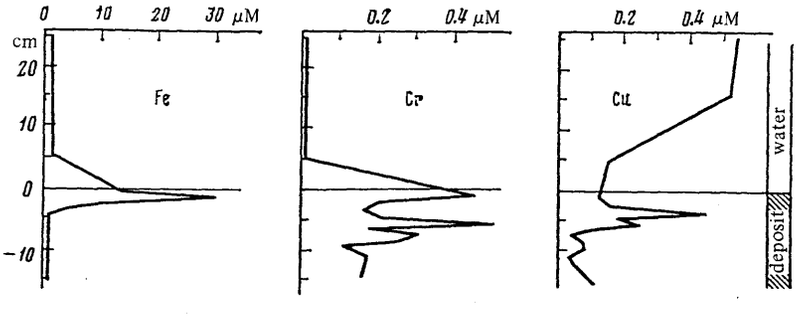



Figure 3. Vertical distribution of Fe, Cr, and Cu in the bottom water and the pore water of the coastal sediments in the Mediterranean.[322]

2,6-di-t-butyl-4-methylphenol and the weakest are mesitylene and *p*-xylene.[357]

In aqueous solutions MeHg(II) has been obtained from Hg(II) also in the presence of methanol, acetic and propionic acids, and aliphatic α-aminoacids (on photolysis), as well as a result of transmethylation:[18,343]

$$Me_3E(IV) + Hg(II) \rightarrow MeHg(II) + Me_2E(IV);\ E = Si, Sn, Pb.$$

The role of such reactions in the geochemical TE cycles is not altogether clear.

### 6. Iron–Manganese Concretions

In connection with the exploitation of the resources of the Pacific Ocean, the autogenic components of its bottom deposits, namely the iron–manganese concretions whose chemistry had been examined previously,[358] have become important. The results of the latest research into the role of TE and their forms in the concretions of the Pacific Ocean are described below.

The density of the concretions can reach 300 units per $m^2$ or 30 kg $m^{-2}$. Their dimensions are on average about 4 cm, but concretions up to 20 cm are encountered. They increase at an average rate from 30 to 300 mm in one million years.[359] Their Mn/Fe ratio varies from 5.6 to 70 and more than 99% of the Mn is in the form of Mn(IV),[360] although the main diagenetic source is probably Mn(II) formed from Mn(IV) in the vicinity of the deposit–water interface.[361] This process is part of the well investigated remobilisation of Mn from deposits,[328,330,362] which exerts a decisive influence on its distribution in bottom waters.

The concretions respond to this remobilisation by a faster increment in their volume on the side in contact with the deposit.[363] This side grows faster, compared with the upper part almost by a factor of 4.[359] A typical concretion consists of two separate non-detritus components having different compositions:[359] the bottom part is enriched in Mn, Mg, Ca, U, and Sb and the upper part in Fe, Ni, Cu, Zn, Co, Th, and the lanthanides. These differences in the chemical compositions of individual parts of the concretions are explained by the variable contributions of the following processes:[364] (1) the hydrogenic process which leads to the direct precipitation or accumulation of colloidal TE oxides from sea water; (2) oxidative diagenesis which takes place in oxidised deposits and tends to increase the content of TE in the concretion; (3) reductive diagenesis, which ensures the reduction of Mn(IV) to Mn(II) by the organic matter with its subsequent reoxidation to Mn(IV). Concretions have also been found in regions with very slow sedimentation of the suspension. In this case the increment in the mass of the concretions takes place at the expense of bottom waters with an increased content of suspended and dissolved TE brought there by bottom streams.[365]

The TE in concretions and also in a series of autogenic minerals (apatite, barite, opal, and carbonate) are mainly concentrated in the aluminosilicate and Mn and Fe oxide phases, owing to the characteristic features of the chemical forms of the TE in sea water and the physicochemical properties of these phases.[366] It has been shown that the TE in a concretion have different oxidation states—for example, Co(III), Pb(II), Pb(IV), and Ti(IV)[367] and Cu(II) and Ni(II).[368]

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Significant advances have been made in recent years in the study of the forms of TE in natural aqueous media. The discovery of the relation between the forms of TE in the abiotic phases of natural aqueous media and their effect on hydrobionts is especially important. However, the experimental data to date are insufficient to reach definite conclusions about the influence of various forms of TE of anthropogenic origin on the health of specific water basins, which is one of the principal tasks of biogeochemistry.

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# The Concept of Vibronic Interactions in Present-day Chemistry

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The present review deals with the chemical aspects of a new concept in the structure and properties of molecules and crystals, namely the concept of vibronic interactions, where the movements of the electrons and the nuclei are not described separately, and account is taken of the mixing of electronic states by the displacements of the nuclei. The applications of this concept to the description of vibronic structure by means of orbital vibronic constants, vibronic reactivity, and chemical activation on coordination, and to electron-conformational interactions, have been examined. The concept of vibronic interactions provides a basis for a deeper understanding of the origins of the structure and transformations of molecular systems.
The bibliography contains 48 references.

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## I. INTRODUCTION

The structure and properties of a molecular system are determined by the motion of its electrons and nuclei, and the interaction between them. The principal laws governing this motion were established in the thirties, immediately after the discovery of quantum mechanics. Because of the mathematical difficulties, restricting but physically justified approximations are introduced in the quantum-mechanical description of the properties of molecules. The most general of these is the Born–Oppenheimer adiabatic approximation (see, for example, Refs.1 and 2), according to which, in view of the very large difference between the masses of the electrons and the nuclei, and hence the appreciable difference in their rates of movement, it is possible to establish the steady motion of the electrons for each instantaneous position of the nuclei. In other words, the electrons follow the motion of the nuclei in inertialess fashion (adiabatically), and the nuclei move in the averaged field created by the electrons.

Thus in this approximation the electrons are assigned only the general ("classical") role of the sources of the average electrostatic field, and the details of the electronic structure do not appear in the description of the motion of the nuclei.

Also in the thirties, some of the most obvious departures from the adiabatic approximation were understood. In 1934, Landau, in a conversation with Teller, first put forward the idea that when there is electronic degeneracy (two or more electronic states with the same energy), the nuclear configuration may be unstable, and undergo spontaneous deformation. This idea, subsequently verified by Jahn and Teller for all types of (non-linear) molecules, formed the basis of the Jahn–Teller theorem, whose consequences are now widely used to analyse the structure and properties of polyatomic systems.[1–5] When the so-called Jahn–Teller effect operates, the electrons do not follow the nuclei adiabatically, and the state of the latter is determined not by the average field of the electrons but by its details, which depend, in particular, on the nature of the degeneracy. The consequent complex relationship between the electronic and nuclear movements is the first and an extremely significant departure from the adiabatic approximation. Cases of degeneracy in the ground state of a molecule are themselves fairly frequent, and their number increases greatly when account is taken of excited states (without which a sufficiently complete study of the structure and properties of molecules is impossible).

In 1957, Opik and Pryce[6] were the first to point out that phenomena analogous to the Jahn–Teller effect may be encountered when there is quasi-degeneracy (pseudo-degeneracy), when for some nuclear configuration of the core of the electronic energy levels are fairly close, but do not coincide as in the case of degeneracy (Jahn–Teller pseudo-effect). The criterion for this pseudo-degeneracy contains the relationship between three parameters of the system, so that the concept of similarity in electron energies becomes relative (see below for more details). Thus the Jahn–Teller pseudo-effect in principle covers all molecular systems, without exception, and the only problem is that in some systems the effect is small and can be neglected.

The theory of the Jahn–Teller effect and pseudo-effect and its applications began to be developed intensively in the early sixties, and has grown into a new field in the physics and chemistry of molecules and crystals, encountered fairly frequently in the literature under the general name of the Jahn–Teller effect (although the term "vibronic effects" is more appropriate). The fields of application of these effects cover the whole of spectroscopy, from Mössbauer via the ultraviolet, visible, and infrared ranges to the entire range of radiofrequency spectroscopy (EPR, NMR, NQR), polarisability and magnetic susceptibility, crystal chemistry, and crystal physics, including such important branches as the nature of the formation of crystal structures, structural phase transformations in ferroelectricity, and reactivity (orbital symmetry rules).

In recent years a new field has begun to develop, in which vibronic interactions are taken into account to explain the origin of the effects of the mutual influence of molecular groups in their chemical binding (coordination), both in the case of chemical reactions and more particularly in the case of the influence of a catalyst.[3,7–10] This trend introduces fundamentally new elements into the allowance for the effects of vibronic interaction, extending them to the case of molecular transformations. With the inclusion of this trend, the approach overall becomes a concept which from a definite viewpoint analyses all the properties of molecules, including their transformations. The mathematical basis of this concept involves abandoning the adiabatic approximation, or taking systematic account of vibronic interactions (see below). To obtain a deeper general understanding of the phenomens, the new concept takes a more systematic account of the role of the electrons and the details of the electronic structure, in the production of the nuclear configuration and its dynamics, and the influence of the latter on the spectral and stereochemical properties and reactivity of molecules.

In a vertain sense, the systematic "introduction" of this concept into chemistry develops a new and more fruitful way of thinking for research workers. In fact, all courses on the structure of molecules present the adiabatic approximation, according to which the electrons follow the nuclei adiabatically, and the nuclei move in the average field of the electrons, and with very few exceptions it is not pointed out that in most cases this picture is incorrect. This creates in research workers a restricting stereotype, according to which the electrons, as already noted, are assigned the classical role of the sources of the electrostatic field, and the extremely important details of the electronic structure of the valence shell related to quantum effects are ignored completely. In the process, the understanding of how changes in the structure of the valence shell of a molecule lead to a change in the nuclear configuration, and a correct understanding of the nature of chemical transformations, are lost. The new concept based on the non-adiabaticity of the interactions of electrons and nuclei (taken into account by the vibronic mixing of different electronic states) directs the thinking of research workers to a more adequate reflection of the structure and properties of polyatomic systems and their chemical transformations.

The present review characterises briefly the essential features of the concept of vibronic interactions and various aspects of its applications in present-day chemistry. The analysis of the latter, for lack of space, has been restricted to examples from chemical reactivity and activation in catalysis, and electron-conformational effects. The review does not deal with the many applications of this concept in spectroscopy, which have developed particularly extensively in the form of new branches of electronic spectroscopy and EPR, or with problems of crystal chemistry, structural Jahn–Teller phase transformations, and ferroelectricity (cooperative effects). These and other interesting aspects of this topic can be found in the literature (see Refs.1–4 and the detailed bibliography in Ref.5).

## II. VIBRONIC INTERACTIONS

The examination of some general equations will help to introduce the terminology and notation. The stationary Schrodinger equation for a molecular system $H\Psi = E\Psi$ can be considered, and the Hamiltonian $H$ represented as the sum of three terms:

$$H = H_Q + H_r + V(r, Q) \qquad (1)$$

where $H_r$ is the part of the Hamiltonian that depends only on the coordinates of the electrons, $H_Q$ the operator of the kinetic energy of the nuclei, and $V(r,Q)$ the operator of the electron–nucleus and nucleus–nucleus interactions ($r$ and $Q$ denote the sets of coordinates of the electrons and nuclei respectively).

It is assumed that a solution of the Schrodinger equation has been found for fixed positions of the nuclei ($H_Q = 0$):

$$[H_r + V(r, Q)]\varphi_k(r, Q) = \varepsilon_k(Q)\varphi_k(r, Q)\,. \qquad (2)$$

In this case the energy levels $\varepsilon_k(Q)$ and wavefunctions $\phi_k(r,Q)$ depend on the coordinates of the nuclei as parameters. The complex wavefunction $\Psi(r,Q)$ can be sought as the expansion with respect to the series of functions $\phi_k(r,Q)$:

$$\Psi(r, Q) = \sum_k \chi_k(Q)\cdot\varphi_k(r, Q) \qquad (3)$$

Substituting $\Psi(r,Q)$ in the equation $H\Psi = E\Psi$ and taking account of Eqn.(2) gives an infinite system of equations for

the functions $\chi(Q)$:

$$[H_Q + \varepsilon_m(Q) - E]\chi_m(Q) - \sum_k A_{mk}\chi_k(Q) = 0$$
$$m = 1, 2, \ldots \quad (4)$$

Here, $A_{mk}$ are the matrix elements of the so-called non-adiabaticity operator. These quantities depend on the derivatives of the functions $\phi_j(r,Q)$ with respect to the coordinates of the nuclei $Q$.[2] This is an effect of non-adiabaticity with the mixing of different electronic states.

If the electronic functions depend little on the coordinates of the nuclei $Q$, the terms $A_{mk}$ in Eqn.(4) are small and can be neglected. The system of equations (4) then takes the form

$$[H_Q + \varepsilon_m(Q) - E]\chi_m(Q) = 0, \; m = 1, 2, \ldots \quad (5)$$

For each electronic wavefunction it is possible to construct $\Psi_m(r,Q)$ as the product

$$\Psi_m(r, Q) = \varphi_m(r, Q)\chi_m(Q) .$$

The function $\chi_m(Q)$ has the significance of the wavefunction describing the motion of the nuclei. This is the adiabatic approximation.

The nature of the adiabatic approximation can be discussed from another viewpoint. The operator $V(r,Q)$ can be expanded in a series with respect to small displacements $Q$ in the region of the point $Q = 0$:

$$V(r, Q) = V(r, 0) + \sum_\alpha \left(\frac{\partial V}{\partial Q_\alpha}\right)_0 Q_\alpha + \frac{1}{2}\sum_{\alpha,\beta}\left(\frac{\partial^2 V}{\partial Q_\alpha \partial Q_\beta}\right)_0 Q_\alpha Z_\beta + \ldots \quad (6)$$

The non-zero terms in this equation (linear, quadratic, etc.) are called the operators of the electronic–vibrational or vibronic interaction. The solution of the electronic Schrodinger equation taking account of only the zeroth term of the expansion (6), $V(r,0)$, gives wavefunctions $\phi(r,0)$ and energy levels $\varepsilon(0)$ which are independent of $Q$ (simple adiabatic approximation). For small displacements of the nuclei $Q$, the dependence of the electronic wavefunction on $Q$ is determined according to perturbation theory by the matrix elements of the linear terms of the vibronic interaction

$$F_\alpha^{(ij)} = \left\langle \varphi_i(r, 0) \left| \left(\frac{\partial V}{\partial Q_\alpha}\right)_0 \right| \varphi_j(r, 0) \right\rangle \quad (7)$$

which are called the linear vibronic constants. Thus the simple adiabatic approximation is equivalent to neglecting the vibronic interaction. On the other hand, systematic allowance for vibronic interaction automatically takes account of non-adiabaticity. It can be shown[2] that the physical significance of this conclusion is preserved in the complete adiabatic approximation.

Thus in the general case, when account is taken of vibronic interaction, the complete wavefunction is represented in the form of Eqn.(3), including excited states. In other words, vibronic interactions "mix" the ground and excited electronic states of the molecule, obtained in the simple adiabatic approximation for fixed positions of the nuclei.

A criterion of the applicability of the adiabatic approximation is provided by the strong inequality

$$\varepsilon_2 - \varepsilon_1 \gg \hbar\omega \quad (8)$$

where $\hbar\omega$ is the quantum of the vibrations in the ground electronic state, and $\varepsilon_2 - \varepsilon_1$ the lowest energy of electronic excitation.

If criterion (8) is fulfilled, then allowance for the vibronic terms in the expansion (6) leads only to small corrections to the quantities found in the adiabatic approximation. If however this criterion is not fulfilled, then allowance for vibronic interactions leads to qualitatively new effects. To classify and analyse these effects it is convenient to use the adiabatic potential surface (or curves), that is the energies of the electronic terms as functions of the nuclear displacements. Fig.1 gives three types of adiabatic potential in the range of the intersection or approach of two electronic terms (for convenience, the one-dimensional case is considered). The greatest breakdown of the adiabaticity criterion takes place when $\varepsilon_2 = \varepsilon_1$ (the case of degeneracy of the electronic state), when the inequality (8) is not fulfilled for any values of $\hbar\omega$. For this case, Jahn and Teller, on the basis of Landau's idea, proved that (in present-day terms) at the point of electronic degeneracy (that is in a nuclear configuration for which the energies of two or several electronic states coincide), the adiabatic potentials do not have a minimum (Fig.1*a*), so that the nuclear configuration is unstable.

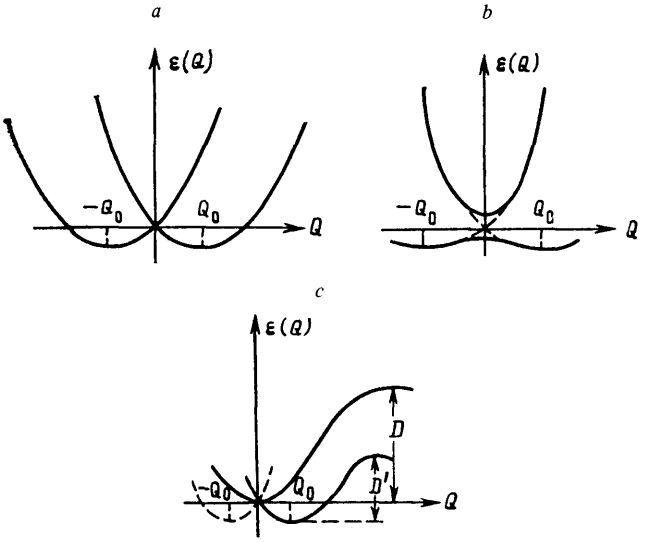



Figure 1. Schematic representation of the three principal cases of vibronic effects: *a*) case of degeneracy (Jahn–Teller effect), *b*) case of pseudo-degeneracy (Jahn–Teller pseudo-effect), *c*) case of electronic rearrangement or vibronic effects at large distances.

Fig.1 also shows that the minima of the adiabatic potential correspond to distorted configurations. This does not mean, however, that it is possible to detect a distorted configuration of the nuclei instead of a highly symmetrical configuration by direct measurements. In fact, there are always two or more of these minima (sometimes an infinite number—a continuum of minima), with equivalent energies, which complement one another in such a way that overall, the original symmetry is preserved. Thus the so-called Jahn–Teller effect reduces not simply to distortion of the geometry of the molecule but to extremely complex nuclear core dynamics which give rise to a whole range of new effects and regularities.[1-5] Because this feature was neglected, until about 1960 all attempts to detect directly the distortions of a system related to the Jahn–Teller effect, generally speaking, were unsuccessful. At about this time, the present author[1-3] observed one of the clearest manifestations of the complex dynamics of molecular systems with allowance

for vibronic effects—the existence of pulsating motions in which molecules spontaneously (and at a definite frequency) change between configurations corresponding to different equivalent minima of the adiabatic potential (similar to those given in Fig. 1*a*). This new phenomenon, together with the observed effects and regularities (and applications) based on it, was registered (in 1978) in the USSR as scientific discovery No. 202.[11]

A situation similar to that arising when $\varepsilon_1 = \varepsilon_2$ is found at a point of the nuclear configuration where the energy levels $\varepsilon_1$ and $\varepsilon_2$ are fairly close to one another (Jahn–Teller pseudo-effect, Fig. 1*b*). Here, together with effects which are consequences of the Jahn–Teller theorem, various new regularities appear.[1-5]

The similarity in energy observed for nuclear displacements in a certain direction $Q$ is fairly characteristic. It was recently shown[12-14] that mixing of the electronic states is the only source of dynamic instability in molecular systems (and that it may be considerable even for large differences $\varepsilon_2 - \varepsilon_1 \cong 10$ eV). This result is important for interpreting the stereochemical properties of molecular systems[3,15] and transition states in chemical reactions,[3,12] and for explaining the nature of structural (including ferroelectric) phase transformations in crystals,[16,17] the "plasticity" of the coordination sphere of certain transition metals, and distortion isomers.[18,19]

Finally, in the last case, illustrated in Fig. 1*c*, there may be effects which appear at large distances from the point of degeneracy (or pseudo-degeneracy). Different situations relating to this case are discussed in more detail below.

## III. DESCRIPTION OF MOLECULAR STRUCTURE BY MEANS OF ORBITAL VIBRONIC CONSTANTS

From the above discussion, it follows that the effects of the vibronic mixing of different electronic states are determined by the vibronic constants (7). These can be written in a more convenient form by making use of the symmetry properties of the molecules. If the coordinates of the displacements of the nuclei used in the expansion (6) are the generalised symmetry coordinates (or normal coordinates) $Q_{\Gamma\gamma}$, which transform as the row $\gamma$ of the irreducible representation $\Gamma$ of the symmetry point group of the molecule, then the linear vibronic constant can be written as

$$F_{\tilde{\Gamma}\tilde{\gamma}}^{(\Gamma\gamma,\Gamma'\gamma')} = \left\langle \Gamma\gamma \left| \left( \frac{\partial V}{\partial Q_{\tilde{\Gamma}\tilde{\gamma}}} \right)_0 \right| \Gamma'\gamma' \right\rangle \qquad (9)$$

where $|\Gamma\gamma\rangle$ and $|\Gamma'\gamma'\rangle$ denote the electronic wavefunctions for fixed positions of the nuclei, transforming as the corresponding rows of the irreducible representation. If the mixed states are not degenerate, then the representations $\Gamma$ and $\Gamma'$ each contain only one row $\gamma$ and $\gamma'$. In this case $\tilde{\Gamma}$ is also non-degenerate, and the symbols for the row $\gamma$ are omitted in $F_{\tilde{\Gamma}}^{(\Gamma,\Gamma')}$. If however one or both of these states is degenerate, then there exist several vibronic constants, corresponding to the number of possible combinations of the rows of the representations. These constants, however, differ from one another only in a numerical factor (the Clebsch–Gordan coefficients), obtainable from Tables.[2,3] Thus the vibronic mixing of two (any) states is described essentially by one vibronic constant.

Some of the vibronic constants have a clear physical significance. In particular, the diagonal linear vibronic constant $F_{\tilde{\Gamma}}^{(\Gamma\Gamma)} \equiv F_{\tilde{\Gamma}}^{\Gamma}$ is equal to the force with which the electronic cloud in the state $\Gamma$ deforms the core in the direction of the symmetrised (normal) displacement $\tilde{\Gamma}$. The molecule is obviously in an equilibrium (but not necessarily stable) state when $F_{\tilde{\Gamma}}^{\Gamma} = 0$ for all $\tilde{\Gamma}$.

In addition to linear vibronic constants, it is possible to introduce quadratic, cubic, etc. vibronic constants. It is possible, for example, to define the quadratic vibronic constants. The general expression for a matrix element of the coefficient of the quadratic terms in the expansion (6) can be written as:

$$K_{0\tilde{\Gamma}\tilde{\gamma}}^{(\Gamma\Gamma')}(\Gamma_1 \times \Gamma_2) = \frac{1}{2} \left\langle \Gamma \left| \left\{ \left( \frac{\partial^2 V}{\partial Q_{\Gamma_1} \partial Q_{\Gamma_2}} \right)_0 \right\}_{\tilde{\Gamma}\tilde{\gamma}} \right| \Gamma' \right\rangle . \qquad (10)$$

Here, the shaped brackets denote tensor convolution, that is a combination of the second derivatives with respect to the coordinates $Q_{\Gamma_1\gamma_1}$ and $Q_{\Gamma_2\gamma_2}$, which transforms as the row $\tilde{\gamma}$ of the representation $\tilde{\Gamma}$ contained in the product of the representations $\Gamma_1 \times \Gamma_2$. The totally symmetric part of the diagonal element (10) denoted $K_{0\tilde{\Gamma}}^{\Gamma}$) has a completely clear physical significance; it defines the curvature of the adiabatic potential (force constant) of the system $K_{\tilde{\Gamma}}^{\Gamma}$, corresponding to the coordinates $Q_{\tilde{\Gamma}}$:[2,3]

$$K_{\tilde{\Gamma}}^{\Gamma} = K_{0\tilde{\Gamma}}^{\Gamma} - 2 \sum_{\Gamma'}{}' |F_{\tilde{\Gamma}}^{(\Gamma\Gamma')}|^2 / \Delta_{\Gamma'\Gamma} \qquad (11)$$

where $\Delta_{\Gamma'\Gamma}$ is equal to half the difference between the energies of the states $\Gamma$ and $\Gamma'$; $\Delta_{\Gamma'\Gamma} = (1/2)(\varepsilon_{\Gamma'} - \varepsilon_{\Gamma})$. Thus keeping for $K_{0\tilde{\Gamma}}^{\Gamma}$ the earlier description as the curvature of the surface or the force constant (the curvature of the surface at the equilibrium point, where $F_{\tilde{\Gamma}}^{\Gamma} = 0$, coincides with the force constant), all the remaining matrix elements (10) (namely the non-totally-symmetric parts $\tilde{\Gamma} \neq A_1$ of the diagonal elements $\Gamma = \Gamma'$ and all the off-diagonal elements) can be called quadratic vibronic constants and denoted $G_{\tilde{\Gamma}}^{(\Gamma\Gamma')}$. $(\Gamma_1 \times \Gamma_2)$.

Similarly, it is possible to derive cubic vibronic constants, some of which (or their combinations) make a direct contribution to the anharmonicity of the system.

An important step towards chemical applications of the theory of vibronic interactions can be taken by introducing orbital vibronic constants. In the molecular orbital (MO) method it is possible to introduce linear, quadratic, etc. vibronic constants for each orbital state. For this purpose the MO energy levels and MO wavefunctions can be denoted $\varepsilon_i$ and $\psi_i(\mathbf{r})$ respectively, and use can be made of the additive operator of the electron–nucleus interaction ($N$ is the number of nuclei):

$$V = \sum_i V_i(\mathbf{r}_i);\ V_i(\mathbf{r}_i) = -\sum_\alpha \frac{e^2 Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} + \frac{1}{N} \sum_{\alpha,\beta} \frac{e^2 Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} . \qquad (12)$$

By analogy with the integral constant (8), the linear orbital vibronic constant (OVC) is then determined from the equation:

$$f_{\tilde{\Gamma}}^{(i)} = \left\langle \psi_i(\mathbf{r}_i) \left| \left( \frac{\partial V_i}{\partial Q_{\tilde{\Gamma}}} \right)_0 \right| \psi_j(\mathbf{r}_i) \right\rangle . \qquad (13)$$

In exactly the same way, by analogy with Eqn. (9), the orbital matrix elements of the quadratic terms of the vibronic interaction are written as:

$$k_{0\tilde{\Gamma}\tilde{\gamma}}^{(ij)}(\Gamma_1 \times \Gamma_2) = \frac{1}{2} \left\langle \psi_i(\mathbf{r}_i) \left| \left\{ \left( \frac{\partial^2 V_i}{\partial Q_{\Gamma_1} \partial Q_{\Gamma_2}} \right)_0 \right\}_{\tilde{\Gamma}\tilde{\gamma}} \right| \psi_j(\mathbf{r}_i) \right\rangle . \qquad (14)$$

Here also, the totally symmetric part of the diagonal element $i = j$ with $\tilde{\Gamma} = A_1$ and $\Gamma_1 = \Gamma_2 = \tilde{\Gamma}$, $k_{0\tilde{\Gamma}}^{(ii)} \equiv k_{0\tilde{\Gamma}}^{i}$ makes a direct contribution to the orbital force constant, and the

non-totally symmetric (for degenerate MO) and off-diagonal elements are the orbital quadratic vibronic constants $g_{\bar{\Gamma}}^{(ij)}(\Gamma_1 \times \Gamma_2)$.

The physical significance of the orbital constants can be considered. First of all it can be seen that the diagonal linear OVC $f_{\bar{\Gamma}}^{(ii)} \equiv f_{\bar{\Gamma}}^{i}$ has the significance of the force with which an electron situated in the $i$th MO deforms the original nuclear configuration in the direction of the symmetrised coordinate $Q_{\bar{\Gamma}}$ (or $Q_{\bar{\Gamma}\bar{\gamma}}$ for degenerate coordinates) minus the corresponding part of the repulsion in this direction (see Eqn.(12)). It is difficult to determine the orbital components directly from experimental data. It is therefore of interest to find the relationship between these orbital contributions and the corresponding integral quantities for the molecule as a whole. This can be done using the combination theorem,[7,9] according to which

$$F_{\bar{\Gamma}\bar{\gamma}}^{\Gamma} = \sum_i q_i^{\Gamma} f_{\bar{\Gamma}\bar{\gamma}}^{i} \qquad (15)$$

where $q_i^{\Gamma}$ represents the occupation numbers of the MO (0, 1, or 2) in the state $\Gamma$ of the molecule. In other words, the total force with which the electron cloud acts on the nuclear core (in a certain direction $Q_{\bar{\Gamma}\bar{\gamma}}$) is equal to the sum of the contributions from each MO. An analogous relationship applies for the diagonal quadratic OVC.

The derivation of the analogous relationships for the off-diagonal OVC is more complicated, since the latter depend on the excited states. In the approximation of "frozen orbitals" (in this approximation, in an excitation $\Gamma \to \Gamma'$ associated with a change in the state of one electron $i \to j$, the states of the other electrons do not change), it has been shown[3] that

$$F_{\bar{\Gamma}\bar{\gamma}}^{(\Gamma\Gamma')} = f_{\bar{\Gamma}\bar{\gamma}}^{(ij)}, \qquad (16)$$

$$K_{\bar{\Gamma}}^{\Gamma} = \sum_i q_i^{\Gamma} k_{\bar{\Gamma}}^{i}, \qquad (17)$$

$$k_{\bar{\Gamma}}^{i} = k_{0\bar{\Gamma}}^{i} - 2\sum_j{}' |f_{\bar{\Gamma}}^{(ij)}|^2/\Delta_{ji} \qquad (18)$$

where $\Delta_{ji} = (1/2)(\varepsilon_j - \varepsilon_i)$.

It can be seen that in the approximation of frozen orbitals, the off-diagonal OVC coincide with the total vibronic constants, and the force constants of the molecule can also be represented additively in terms of the orbital contributions, although the latter also involve other orbitals. Analogous equations can be derived for the cubic and other contributions of higher orders.

The orbital vibronic constants supplement the data on the electronic structure of molecules in the one-electron MO approximation (the set of one-electron energy levels and wavefunctions is a stationary or static picture) with important information on the action of the electrons on the nuclear core (the dynamic picture). The description of the electronic structure of molecules in MO terms is at present the most adequate and the most easily applied in practice. It can be used to analyse chemical processes in convenient and clear terms, facilitating a deeper understanding of their nature. In this approximation, however, no account is taken of the influence of the electron cloud on the positions of the nuclei, so that it is not clear whether the configuration of the nuclei will be the equilibrium configuration for the given electron distribution. Moreover, this static picture does not indicate how the configuration of the nuclei changes with change in the electronic structure.

Allowance for the vibronic constants makes it possible to eliminate most of this unsatisfactory feature of the description of the electronic structure: the integral vibronic constants characterise the deforming forces and force constants corresponding to the given electronic structure. The orbital vibronic and force constants characterising the contributions of the individual MO to these dynamic characteristics are particularly useful. Knowing the orbital vibronic and force constants, it is possible to predict the behaviour of the nuclear core with change in the electronic structure: the change in its equilibrium configuration, force constants, anharmonicity constants, etc. These data can be used to predict the nature of the change in reactivity. Thus the orbital and vibronic and force constants supplement considerably the static description of the electronic structure in the MO approximation.

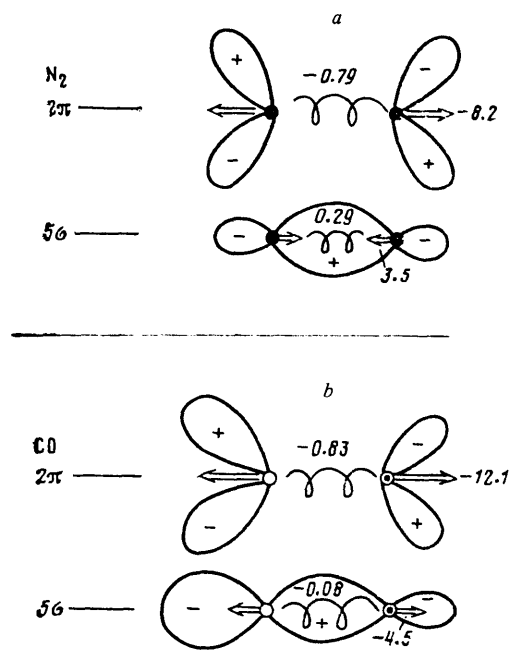



Figure 2. Illustration of the vibronic structure of molecules: *a*) 5σ HOMO (bonding) and 2π LUMO (antibonding) of the $N_2$ molecule; *b*) HOMO and LUMO of the CO molecule; HOMO—weakly antibonding, LUMO—strongly antibonding. The contribution of the orbital electrons to the deforming force is shown by arrows, figures in $10^{-4}$ dyn; the contribution to the force constant is shown by the spring, figures in $10^6$ dyn cm$^{-1}$.

In Fig.2, the concept of the structure of polyatomic systems described above is illustrated for the highest occupied MO (HOMO) 5σ and the lowest unoccupied MO (LUMO) 2π of the simplest diatomic molecules $N_2$ and CO (the numerical characteristics of these MO are discussed in section IV). Fig.2 shows that in the $N_2$ molecule, the electron in the 5σ MO "attracts" the nuclei with a force $f_R^{5\sigma}(N_2) = 3.51 \times 10^{-4}$ dyn

($R$ is the distance between the nuclei), whereas in the CO molecule the electron in the analogous orbital "repels" the nuclei with a force $f_R^{5\sigma}(CO) = -4.5 \times 10^{-4}$ dyn. The electrons in the $2\pi$ orbitals "repel" the nuclei with a force $f_R^{2\pi}(N_2) = -8.18 \times 10^{-4}$ dyn and $f_R^{2\pi}(CO) = -12.1 \times 10^{-4}$ dyn.

The contributions to the force constant (shown as springs in Fig.2) have the following values (dyn cm$^{-1}$):

| | $5\sigma$ | $2\pi$ |
|---|---|---|
| $N_2$ | $0.23 \cdot 10^{-6}$ | $-0.73 \cdot 10^{-6}$ |
| CO | $0.08 \cdot 10^{-6}$ | $-0.83 \cdot 10^{-6}$ |

These data show first of all that the $5\sigma$ orbital in the $N_2$ molecule is bonding, and that in CO is antibonding, whereas the $2\pi$ MO are antibonding in both molecules. Moreover, the above data contain quantitative information on the degree of bonding or antibonding character of each MO and its contribution to the deforming force and the force constant of the bond. As already noted, this information is particularly valuable in the analysis of the influence of the rearrangement of the electron cloud on the behaviour of the nuclear core (see section IV).

In the case of polyatomic molecules, the orbital and force vibronic constants carry much richer information than the simple representation of the bonding or antibonding character of the MO. Thus in accordance with the rules of group theory, the orbital linear vibronic constant $f_{\bar{\Gamma}}^{(ij)} = \langle i | (\partial V / \partial Q_{\bar{\Gamma}})_0 | j \rangle$ is non-zero if the product of the representations $\Gamma_i$ and $\Gamma_j$ according to which the $i$th and $j$th MO transform, contains the representation $\bar{\Gamma}$ corresponding to the symmetrised direction $Q_{\bar{\Gamma}}$. For different $\Gamma_i$ and $\Gamma_j$, the representation $\Gamma$ can be any one. For $i = j$ the representation $\Gamma$ is contained in the symmetrised square $[\Gamma_i \times \Gamma_i]$, so that if the $i$th MO is non-degenerate, the representation $\bar{\Gamma}$ is totally symmetric. In other words, the electrons in the non-degenerate MO deform the molecule without changing its symmetry. The MO are also bonding or antibonding, depending on the sign of $f_{\bar{\Gamma}}^{ii}$. For degenerate MO the product $\Gamma_i \times \Gamma_j$ contains not only the totally symmetric but also non-totally symmetric representations, so that the electrons in the degenerate MO can deform the molecule with a change in its symmetry (in complete correspondence with the Jahn–Teller theorem[2]). Moreover, in accordance with Eqn.(18), which contains $f_{\bar{\Gamma}}^{(ij)}$, the "softening" of the molecule brought about by the orbital electron can take place in any direction (depending on the mixed states $i$ and $j$ with small $\Delta_{ji}$).

## IV. VIBRONIC REACTIVITY AND CHEMICAL ACTIVATION ON COORDINATION IN CATALYSIS

Vibronic effects may have a significant influence on the reactivity of a molecular system. Thus as can be seen, for example, from Eqn.(11), as a result of vibronic mixing the curvature of the adiabatic potential of the ground state decreases by an amount $F^2/\Delta$. This decrease in the curvature of the adiabatic potential surface evidently leads to a decrease in stability (in the limit ($F^2/\Delta > K_0$) the system becomes unstable) and to an increase in reactivity.

This last statement requires explanation. First of all it is necessary to give a quantitative definition of the reactivity of molecules, and even this is an extremely difficult task. Reactivity should obviously characterise the rate of the elementary act of a chemical reaction, so that it is natural to try to relate it to the activation energy of the reaction. The latter, however, may depend not only on the given molecule but also on the molecule with which it reacts.

In the study of the change in the reactivity of a given molecule under the influence of vibronic effects or a change in its electronic structure, a measure of its reactivity in a given chemical reaction is provided by the quantity $D$, the activation energy of the given reaction, associated with the activation of the molecule being considered (see the discussion in Refs.3 and 10). To determine $D$ it is necessary to know the ascending section of the potential energy curve along the reaction coordinate from its minimum to the maximum of the barrier. Comparison of these sections, constructed with and without allowance for vibronic effects, other conditions being equal, shows that the vibronic effects decrease considerably the activation energy of the reaction taking place along the coordinate $Q$ active in the Jahn–Teller effect or pseudo-effect, that is along the displacements of the nuclei for which the vibronic mixing of the electronic states is a maximum.

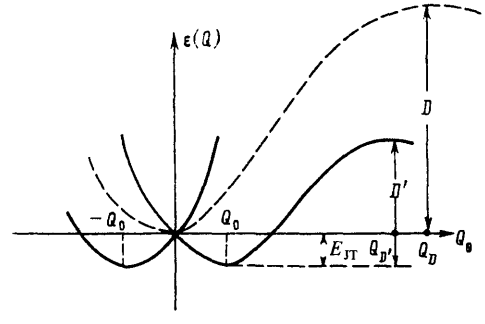



Figure 3. Adiabatic potential in the direction of the coordinate $Q_\theta$ active in the Jahn–Teller effect, at large distances, illustrating the lowering of the activation energy $\Delta D = D' - D$ for the reaction taking place in this direction, compared with the same reaction in the absence of the Jahn–Teller effect (broken curve).

This conclusion is illustrated in Fig.3 for the case where there is a Jahn–Teller effect in the original highly symmetrical nuclear configuration $Q = 0$, and the system at this point does not have an energy minimum with respect to the nuclear displacements described by the generalised coordinate $Q$; the displacements at the point $Q = \pm Q_0$ at which the initial nuclear configuration is distorted have minimum values. It can readily be seen that the change in the activation energy in this case may be considerable, since the points $Q_0$ and $Q_D$ are not very far from one another (the distortions due to the Jahn–Teller effect are of the order of tenths of an Ångstrom unit, and the distances to the activation barrier are usually greater, but not by much; in any case, they are quantities of the same order of magnitude).

An example is provided by substitution or unimolecular decomposition in an octahedral complex of a transition metal having a doubly degenerate $E$ term, for example for copper(II), for which a strong Jahn–Teller effect is observed. As a result of the Jahn–Teller effect, the adiabatic potential of the system has three minima,[1-4] at which the octahedron is elongated along a tetragonal axis so that the two ligands on the four-fold axis are at a greater distance than the other four. In the tetragonal coordinates $Q_\theta$ and $Q_\varepsilon$,[1,2]

the distortion (elongation of the octahedron) takes place along the coordinate $Q_\theta$, which is thus the coordinate along which the activation energy of the reaction decreases (relative to the other directions, other conditions being equal).

Thus these reactions should take place in the direction of the displacements $Q_\theta$ for which the two axial ligands move apart (and the four equatorial ligands approach one another). For a unimolecular reaction, this means the dissociation of two ligands in the *trans*-position, and for substitution it means the replacement of these two ligands, giving *trans*-substituted complexes. In other words, when elongated octahedra are formed (during the pulsations), the two ligands in the *trans*-position are less strongly held and are more susceptible to attack by substituting reagents.[20]

This result agrees completely with available experimental data obtained in the study of the behaviour of octahedral complexes of copper(II) in solution or in the gas phase. Thus these complexes first lose two ligands in the *trans*-position to give a square-planar structure, and substitution reactions give only *trans*-substituted complexes (an exception is provided by bidentate ligands, which can only form bonds in two *cis*-positions). On the other hand, it can readily be seen that in this system, if other conditions are equal the Jahn–Teller effect is suppressed, the rate of replacement is lowered considerably; this has also been confirmed experimentally.[21] According to the theory, similar effects should be expected for octahedral complexes of $Cr^{II}$, $Mn^{II}$, $Ag^{II}$, and other systems with an $E$ term.

Other terms (or other nuclear configurations with an $E$ term) will correspond to other mechanisms of this reaction. They can be examined qualitatively from the distortions expected as a result of the Jahn–Teller effect and pseudo-effect. In particular, for a tetrahedral system with a $T$ term (of the type $CH_4^+$), which as a result of the Jahn–Teller effect should be expected to give four minima of the adiabatic potential with one elongated bond and three shortened bonds, dissociation and replacement with a lowered activation energy can be expected at this elongated bond.

In some cases it is possible to obtain quantitative estimates of the change in the reactivity of molecules (the decrease in the activation energy of the chemical reaction) as a result of vibronic interactions.[7–10] The above example of an octahedral system with an $E$ term can be considered. To analyse the ascending part of the adiabatic potential along the reaction coordinate, it can be approximated by a polynomial of the third degree:[3,7–10]

$$\varepsilon(Q) = aQ + bQ^2 + cQ^3 \ . \qquad (19)$$

Without allowance for vibronic effects, the curve has a minimum at the origin of coordinates, and $\varepsilon(Q)$ is described by the expression

$$\varepsilon(Q) = \frac{1}{2}KQ^2 - \gamma Q^3 \qquad (20)$$

where $K$ is the force constant, and $\gamma$ takes account of the deviations from harmonicity. With allowance for vibronic effects, the curve has the form

$$\varepsilon'(Q) = FQ + \frac{1}{2}K'Q^2 - \gamma' Q^3 \qquad (21)$$

where $F$ is the linear vibronic constant corresponding to the Jahn–Teller effect, which for the case of an $E$ term is related to the stabilisation energy $E_{JT}$ (Fig. 3) by the relationship: $E_{JT} = F^2/2K$.

In the case being considered, the greatest contribution to the change in the form of the adiabatic potential along the coordinate $Q_\theta$ is made by the linear terms of the vibronic interaction.[2] To estimate the effect, therefore, the changes in the force constant and the anharmonicity constant in this direction are neglected. In this case $K' = K$ and $\gamma' = \gamma$, and the change in the activation energy $\Delta D = D' - D$ is given by the following expression (more detailed calculations are given below):

$$\frac{\Delta D}{D} = -3p\left(1 - p + \frac{p^2}{3}\right) \qquad (22)$$

where $p = (4E_{JT}/3D)^{1/2}$.

It can be seen that the change in the activation energy as a result of the Jahn–Teller effect is considerable. For example, for $E_{JT}/D = 0.1$, $(\Delta D/D) \cong 0.7$, that is the activation energy is lowered by 70%. It should be emphasised that this decrease in the activation energy takes place only in a definite direction, namely in the direction of the coordinates active in the Jahn–Teller effect or pseudo-effect (in the case being considered in the direction of the coordinate $Q_\theta$ for which two ligands in the *trans*-position are moved apart). Thus when there are strong vibronic effects in one or both reacting systems, the reaction mechanism is dictated by these effects.

The following general question arises from the vibronic reactivity examined above. If it is known how the vibronic effects, by decreasing the stability, increase the reactivity, that is lower the activation energy of chemical reactions in definite directions, is it not possible to change the reactivity of a molecule in a required direction by external influences (perturbations)? In other words, knowing the vibronic structure, it might be possible, using the concept of vibronic interactions, to develop methods for the vibronic activation of molecular systems. It is possible to given an affirmative answer to this question, and one method of studying the chemical activation of molecules, based on vibronic theory, is examined below.

The orbital vibronic constants introduced in section III, and the picture of the vibronic structure of molecules developed from it, provide a good base for a new approach to the problem of chemical transformations, and in particular to a deeper understanding of the nature and to a semi-quantitative description of the action of one molecular system on the reactivity of another during the reaction between them.[7–10,22–24] This last feature is particularly important in catalysis, where the coordination of a reagent molecule to the active centre of a catalyst (homogeneous or heterogeneous) leads to a marked change in its activity (reactivity) with respect to the chemical reaction with another atom or molecule (or unimolecular decomposition). In view of the importance of this catalytic aspect of the problem and to introduce a more specific content, the discussion here will deal chiefly with the problem of the activation of molecular systems in their reaction with a catalyst, although, as shown below, the proposed approach can also be applied to other aspects of the problem of molecular transformations.

As noted above, the diagonal linear orbital vibronic constant $f^i_{\bar{\Gamma}\bar{\gamma}}$ characterises the force with which an electron in the $i$th MO deforms the core in the direction of the symmetrised displacements $Q_{\bar{\Gamma}\bar{\gamma}}$, minus the fraction of the nuclear repulsion force in this direction corresponding to one electron. The total force deforming the molecule in this direction (the integral diagonal vibronic constant $F^\Gamma_{\bar{\Gamma}\bar{\gamma}}$) in the state $\Gamma$ is determined by the combination rule (15), from which it can be seen that if the system in the given configuration of the nuclei in the direction of the symmetrised coordinate $Q_{\bar{\Gamma}\bar{\gamma}}$ is stable, the following equality applies

$$F^\Gamma_{\bar{\Gamma}\bar{\gamma}} = \sum_i q^\Gamma_i f^i_{\bar{\Gamma}\bar{\gamma}} = 0 \qquad (23)$$

that is the generalised forces produced as a result of the action of the electrons on the nuclear configuration in the direction $\bar{\Gamma}\bar{\gamma}$ are compensated at the equilibrium point, although for each MO this force, generally speaking, is non-zero, and the forces $f^i$ are different for different orbitals (the force of nuclear repulsion in a given direction for a given nuclear configuration is constant, and is independent of the orbital, whereas the electron distribution changes significantly from one orbital to another).

It can be seen from Eqns.(17) and (18) that formally, there is also a combination rule for the orbital force constants: the curvature of the adiabatic potential surface in a given direction $K_{\bar{\Gamma}}^{\Gamma}$ is equal to the sum of the orbital contributions $k_{\bar{\Gamma}}^{i}$. Unlike the linear vibronic constants, however, the force constant $k_{\bar{\Gamma}}^{i}$ is determined not only by the given orbital but also by the contributions of vibronic mixing with other orbitals. Of the latter, it is necessary to take into account only the unoccupied or partly occupied orbitals, since the contributions of the vibronic mixing of completely filled orbitals appear twice with opposite signs in the expression for $K_{\bar{\Gamma}}^{\Gamma}$, and compensate one another.

Any effect of a given molecular system on another (van der Waals interaction, hydrogen bonding, static polarisation, chemical bonding with sharing of electrons, oxidation, reduction, excitation, ionisation, coordination) begins with a change in the less inert (more mobile) electron distribution in it, which then leads to changes in the more inert nuclear configuration. If the change in the electronic structure is sufficiently small, it can be described in a first approximation by the change in the electron populations of the MO, $\Delta q_i$. So long as the values of $\Delta q_i$ are not too large (of the order of one electron), it is possible, in Koopmans' approximation (the approximation of frozen orbitals), to use this description (in fact, as a result of the change in the interelectronic repulsion, change in $q_i$ also leads to a change in the wavefunctions of the MO, but this effect is of second order with respect to $\Delta q_i$; it can be included at the cost of a marked increase in the complexity of the equations).

The new values of the orbital populations $q_i^{\Gamma} + \Delta q_i$ naturally lead to a change in the electron distribution and to decompensation of the orbital deforming forces and force constants. Thus if initially the system was in equilibrium with $F_{\bar{\Gamma}} = 0$ and $K_{\bar{\Gamma}} > 0$ (here and subsequently, for convenience, the index of the state $\Gamma$ is omitted), then replacing $q_i$ by $q_i + \Delta q_i$ in Eqns.(15) and (17) gives (here and subsequently, $q$ is in units of e)

$$F_{\bar{\Gamma}} = \sum_i \Delta q_i f_{\bar{\Gamma}}^{i} , \qquad (24)$$

$$\Delta K_{\bar{\Gamma}} = K'_{\bar{\Gamma}} - K_{\bar{\Gamma}} = \sum_i \Delta q_i k_{\bar{\Gamma}}^{i} + \sum_{i,j}{}' q_i \Delta q_j |f_{\bar{\Gamma}}^{(ij)}|^2/\Delta_{ji} . \qquad (25)$$

Thus a rearrangement of the electron cloud in which there is a change in the populations of some orbitals produces a non-zero deforming force $F_{\bar{\Gamma}}$ in the symmetrised direction $Q_{\bar{\Gamma}}$; in this direction the corresponding $f_{\bar{\Gamma}}^{i}$ (for which $\Delta q_i \neq 0$) are non-zero (deforming effect), and the force constant changes by $\Delta K_{\bar{\Gamma}}$ (softening effect). It can immediately be stated how the direction of the deforming force depends on the symmetry of the $i^{\text{th}}$ orbital, which transforms according to the representation $\Gamma_i$: as already noted $f_{\bar{\Gamma}}^{i}$ is non-zero if $[\Gamma_i \times \Gamma_i]$ contains $\bar{\Gamma}$. If $\Gamma_i$ is not degenerate, then $\bar{\Gamma}$ can only be totally symmetric, that is non-degenerate MOs deform the molecule only along the totally symmetric displacements, without changing their symmetry. For non-degenerate $\Gamma_i$ the representation $\bar{\Gamma}$ may also be non-totally-symmetric, but only in the same way as in the Jahn–Teller effect.[2] $\bar{\Gamma}$ for $\Delta K_{\bar{\Gamma}}$ may be either, particularly as a result of the second term of the sum (25), in which $f_{\bar{\Gamma}}^{(ij)}$ is non-zero if $\bar{\Gamma} \quad \Gamma_i \times \Gamma_j$. Analogous equations can be written for the change produced by electron rearrangement in the anharmonicity constants, etc.

The deforming forces and the changes in the force constants and anharmonicity constants produced under the influence of electron rearrangement explain naturally the change in the reactivity of the molecule and its activation, and, when the changes are sufficiently large, its chemical transformation. It will be shown below how it is possible to determine approximately the quantitative dependence of these changes on the degree of electron rearrangement. However, from Eqns.(20) and (21), it is already possible to reach various general conclusions about the conditions corresponding to the greatest influence of electron rearrangement in coordination. Thus it follows from these equations that the deforming and softening effect of the coordination centre on a given molecule is linearly dependent on the orbital charge transfer $\Delta q_i$. The total transfer $\Delta q = \sum_i \Delta q_i$ cannot be large, from thermodynamic considerations. Thus the values of $\Delta q_i$ can in principle be large if bond formation between the coordination centre and the given molecule involves more than one orbital and if $\Delta q_i$ have different signs for different orbitals.

In the case, frequently encountered, where the orbitals most active in chemical bond formation are two in number, namely the bonding HOMO (for which $f^{(1)} > 0$) and the antibonding LUMO ($f^{(2)} < 0$), the orbital charge transfers have different signs: $\Delta q_1 < 0$ and $\Delta q_2 > 0$. Overall, for example, the deforming force from Eqn.(24) is equal to:

$$F = \Delta q_1 f^{(1)} + \Delta q_2 f^{(2)} = -(|\Delta q_1 \| f^{(1)}| + |\Delta q_2 \| f^{(2)}|) , \qquad (26)$$

In other words, in this case the sum of the absolute magnitudes of the contributions of the two orbitals is taken (the situation for the contributions to the change in the force constant $\Delta K$ is analogous). Thus the greater the absolute magnitude of the orbital charge transfers of different sign, the greater the effect of one molecule on the other in the case being considered. When more than two orbitals are active in bond formation, the number of favourable combinations increases with increase in the vibronic influence, but the total transfer $\Delta q$ remains small. This leads to a conclusion about the role of many-orbital bonds in the vibronic effect of one system on another (in particular in catalysis). From this viewpoint, the unique role of transition metals (and lanthanides) in catalysis is attributed to the possible formation of many-orbital bonds by these elements and their compounds with other molecular formations.

If the resulting deforming force $F$ and the change in the force constant $\Delta K = K' - K$ and the anharmonicity constant $\gamma' - \gamma$ are known, Eqns.(20) and (21) can be used to obtain the following relationships ($Q_0$ is the displacement of the minimum of the potential energy curve as a result of the action of the deforming force $F$, and $Q_D$ and $Q_D$, the positions of

the maxima of the barrier before and after coordination; see Fig. 3): [7-10]

$$D = K^3/54\gamma^2;\ Q_D = K/3\gamma = (6D/K)^{1/4};\ Q_{D'} = K'/3\gamma' - Q_0 \qquad (27)$$
$$Q_0 = (K'/6\gamma')\{1 - [1 + (12\gamma' F/(K')^2]^{1/4}\},$$

$$D' = (K' - 6\gamma' Q_0)^3/54(\gamma')^2 = (K')^3/54(\gamma')^2 - K'Q_0/3\gamma' + 2K'Q_0^2 - 4\gamma' Q_0^3$$
$$\Delta D = D' - D = -D[1 - (K'/K)^3(\gamma/\gamma')^2] - (K')^2 Q_0/3\gamma' + 2K'Q_0^2 - 4\gamma' Q_0^3. \qquad (28)$$

The last equation can be simplified. The coefficients of the cubic terms $\gamma$ can be expressed in terms of the spectroscopic corrections for anharmonicity $\omega x$, [25] which in many cases are known from experimental data. Thus $\gamma/\gamma' = \beta^{1/2}(K/K')^{3/2}(\hbar\omega'/\hbar\omega) = \beta^{1/2}(K/K')$, where $\beta = \omega x/\omega' x'$ (when the electron rearrangements are not too great, $\beta$ is close to 1). Finally:

$$\Delta D = -D[1 - \beta(K'/K)] - K'Q_0(6\beta KD)^{1/2}/K + 2K'Q_0^2[1 - 2KQ_0(54\beta KD)^{-1/2}] \qquad (29)$$

This equation makes it possible to calculate the change in the activation energy $\Delta D$ for the reaction being considered with a given $D$, if the values are known for the vibronic constants and the changes in the electron populations in the electron rearrangement, in terms of which $K'$, $Q_0$, and $\beta$ are defined. Eqn. (29) can also be regarded as an empirical equation relating $\Delta D$ to the experimentally observable parameters of the molecule $K$, $K'$, $Q_0$, and $\beta$.

For a complex molecule with many degrees of freedom, these discussions and conclusions relate to each normal coordinate, and in partiular to that along which the reaction being considered takes place (which may be a linear combination of normal coordinates). In these multidimensional cases, the equations given above can also be used to determine the change in the geometry of the molecule with change in the electronic structure.

Eqn. (29) is approximate, and has meaning only when the changes in the electronic structure relative to the original structure are not too large and have not yet led to the formation of an essentially new molecular system. These electron rearrangements take place in the above-mentioned processes of oxidation, reduction, exitation, ionisation, and coordination of a given molecule to another (in a chemical reaction, as a ligand in coordination systems, on a solid surface during adsorption in heterogeneous catalysis), etc.

The last cases, which can be combined under the general term of activation on coordination, are particularly important. Here, the values of the changes in the MO populations due to charge transfer to and from the coordination centre are fractional. Cases of the transfer of integral charges (in oxidation, reduction, ionisation, excitation, etc.) can in principle be studied by other methods (for example by calculating the total electronic structure of the initial and final systems), but the analysis of the change in the properties of a system with fractional charges can apparently be carried out only by the method examined, with the introduction of orbital vibronic constants.

The assumption that the change in the electronic structure on coordination is slight is justified in most cases; this is confirmed by spectroscopic studies, which indicate that the molecule for the most part retains its individual characteristics, which are not too greatly changed under the influence of coordination. This does not apply to such cases, as for example, the coordination of the $H_2$ molecule when it dissociates completely, although in these cases, the above method can also be used to determine qualitatively the direction in which the initial stage of the process takes place (for example to explain why and predict when $H_2$ will dissociate on coordination).

The practical application of the equations obtained requi suitable methods for determining the parameters appearing them. It follows from Eqn. (29) that the change in the activation energy of a chemical reaction with another molecule with change in the electronic structure of a given molecule, including its coordination to any coordination centre, depends on the parameters of the molecular orbital structure of the activated molecule, including the vibronic constants and the change in the MO populations $\Delta q_i$. In the general case, $\Delta q_i$ are determined not only by the electronic structure of the given molecule but also by the state of the coordination centre and the coordination geometry. The latter determines which orbitals of the molecule, overlapping the orbitals of the centre, undergo the greatest change in population $\Delta q_i$.

From general considerations, confirmed by specific calculations, it follows that, apart from certain special cases, the greatest changes when simple molecules are coordinated are undergone by only two orbitals, the HOMO and the LUMO. If the change in the populations of the inner orbitals is neglected, Eqns. (24) and (25) are simplified considerably, and they can be written in the following form (the superscripts 1 and 2 refer to the HOMO and LUMO respectively):

$$F = f^{(1)}\Delta q_1 + f^{(2)}\Delta q_2, \qquad (30)$$

$$\Delta K = k^{(1)}\Delta q_1 + k^{(2)}\Delta q_2, \qquad (31)$$

$$\beta - 1 = C^{(1)}\Delta q_1 + C^{(2)}\Delta q_2. \qquad (32)$$

The force constants $k^{(1)}$ and $k^{(2)}$ introduced are combinations of the corresponding vibronic constants, and they show how the force constant will change when one electron is added to the corresponding orbital. The last equation, like the first two, describes the linear dependence of the ratio of the anharmonicity constants on the charge transfer $\Delta q_i$; the coefficients $C^{(1)}$ and $C^{(2)}$ are complex combinations of the cubic orbital vibronic constants (and orbital vibronic constants of lower degrees).

All six coefficients ($f^{(1)}$, $f^{(2)}$, $k^{(1)}$, $k^{(2)}$, $C^{(1)}$, and $C^{(2)}$) can readily be calculated if the values of $F$, $\Delta K$, and $\beta$ are known for any two independent electron rearrangement processes (for two pairs of values of $\Delta q_1$ and $\Delta q_2$, except the trivial case $\Delta q_1 = \Delta q_2 = 0$). These processes may be, for example, ionisation ($\Delta q_1 = -1$, $\Delta q_2 = 0$), reduction ($\Delta q_1 = 0$, $\Delta q_2 = 1$), or excitation ($\Delta q_1 = -1$, $\Delta q_2 = 1$), so long as the corresponding empirical parameters are known. For the deforming force $F$, Eqn. (36) gives

$$F = -K'Q_0[1 - KQ_0(6\beta KD_0)^{-1/4}] \qquad (33)$$

where $K$ and $D_0$ are the constants for the non-perturbed molecule ($D_0$ is the dissociation energy of the molecule in the direction being considered), and $K'$, $Q_0$, and $\beta$ relate to the molecule which has undergone electron rearrangement.

The force constants $K$ and $K'$ are readily found from the corresponding vibration frequencies. It is more difficult to determine the deformation of the molecule $Q_0$ in the direction $Q$; direct X-ray diffraction data are not always available. For simple electron rearrangements such as ionisation or excitation, $Q_0$ can be determined from spectroscopic data. In a number of cases, particularly for simple molecules, $Q_0$ can be determined from the known value of $K'$, using empirical relationships between them (see for example Ref. 26). In this case the theory becomes one-parameter; [23,24] all the quantities are determined by one parameter, namely the change in the corresponding vibration frequency in the coordinated state. This version is best in the parametrisation of the theory being considered, since in the experimental

determination of $Q_0$, for example by X-ray diffraction, the formation of the lattice may influence its numerical value, with a significant effect on the results (the value of $Q_0$ must be known with a relatively high accuracy).

Knowing the coefficients in Eqns.(30)–(32), it is possible to use the charge transfer to determine the deforming force and the changes in the force constant and the anharmonicity constant in the direction of the chemical reaction, and then to use Eqn.(29) to estimate the change $\Delta D$ as a function of $D$. On the other hand, if $F$ and $\Delta K$ are known for the perturbed molecule, it is possible to determine $\Delta q_1$ and $\Delta q_2$ for the HOMO and LUMO.

As already noted, Eqn.(29) can also be used as an empirical relationship between $\Delta D$ and $D$:

$$\Delta D = aD + bD^{1/4} + c + dD^{-1/4} \qquad (34)$$

where the coefficients $a$, $b$, $c$, and $d$ are determined from the known empirical parameters $K$, $K'$, and $Q_0$, and $\beta$. Frequently, the value of $D$, that is the activation energy of the reaction being considered in the absence of a catalyst, is unknown. In these cases it is possible, by constructing the $\Delta D = f(D)$ curves for each coordination centre (or any other source of electron rearrangement), to compare them with one another and to determine the relative efficiency of different centres (or sources) for each value of $D$.

Specific examples can be considered. The electronic structure and spectroscopic parameters of the CO molecule have been well studied, so that it is comparatively easy to determine its fundamental vibronic constants and force constants. Its HOMO is the $5\sigma$ orbital, and the LUMO the $2\pi$ orbital. Knowing from experimental data the values of $K$ for the original CO molecule and the values of $K'$, $\beta$, and $Q_0$ for the ionised molecule $CO^+$ [25,27] ($\Delta q_1 = -1$, $\Delta q_2 = 0$) and for the excited state of CO ($5\sigma^2 2\pi^0 \rightarrow 5\sigma^1 2\pi^1$ transition; $\Delta q_1 = -1$, $\Delta q_2 = 1$), [26,28] it is possible to obtain from Eqns. (30)–(32) the following values (for the configurations $5\sigma^1 2\pi^1$, the average values for the two terms $A\,^1\Pi$ and $a\,^3\Pi$ were used):

$$\begin{array}{ll} f^{(1)} = -4.54\cdot10^{-4}\ \text{dyn} & f^{(2)} = -12.1\cdot10^{-4}\ \text{dyn} \\ k^{(1)} = -0.080\cdot10^{6}\ \text{dyn cm}^{-1} & k^{(2)} = -0.83\cdot10^{6}\ \text{dyn cm}^{-1} \\ C^{(1)} = 0.134 & C^{(2)} = 0.0104 \end{array} \qquad (35)$$

The values of both the vibronic constants and the force constants show that both orbitals ($5\sigma$ and $2\pi$) are antibonding, the latter being much more antibonding than the former. Unlike the qualitative picture of the nature of the corresponding orbital (antibonding or bonding), which can often (but not always) be obtained without using the vibronic approach, the latter, as can be seen from the figures obtained, makes it possible to determine quantitatively the degree of participation of the corresponding orbital in the deforming force and the force constant.

Knowing the constants (35), it is possible to analyse the behaviour of the carbon monoxide molecule in any other situation, in particular when coordinated. If the charge transfer $\Delta q_1$ and $\Delta q_2$ resulting from coordination is known, it is possible to determine the values of $F$, $\beta$, and $\Delta K$, and hence $\Delta D$ (for a given $D$), and conversely. The values of these constants show that the negative (antibonding, and hence decreasing the activation energy) force $F$ and the negative $\Delta K$ (acting in the same direction) will be greater, the greater the positive values of $\Delta q_1$ and $\Delta q_2$, that is the greater the increase in the populations of the HOMO and LUMO. Since the HOMO is completely occupied by electrons, however, $\Delta q_1$ may be either zero or negative. Thus the activation of CO will be greater, the greater $\Delta q_2$ and the smaller the absolute magnitude of the negative $\Delta q_1$, so that, for example, for linear coordination the catalyst of the corresponding reactions will be more effective, the stronger its $\pi$-donor properties and the weaker its $\sigma$-acceptor properties.

The linear coordination of CO to a nickel atom on an NiO surface can be considered. Experimental data for this system give the value $K' = 1.710 \times 10^6$ dyn cm$^{-1}$, [27] and the relationship between $K'$ and $Q_0$, [25] namely $K' = (1.7957 - 8.2926\,Q_0\,[\text{Å}]) \times 10^6$ dyn cm$^{-1}$, can be used to obtain $Q_0 = 0.0126$ Å, $F = -2.119 \times 10^{-4}$ dyn, and $\Delta K = K' - K = -0.192 \times 10^6$ dyn cm$^{-1}$; Eqns.(30)–(32) then give $\Delta q_1 \cong -0.32$, $\Delta q_2 \cong +0.26$, and $\beta = 0.93$. This gives the details of the mechanism of the activation of CO on nickel oxide: coordination is accompanied by the transfer of an electron charge of ~0.3 e to the metal from the weakly antibonding $5\sigma$ orbital of CO, and by approximately the same transfer of charge from nickel to the strongly antibonding $2\pi$ orbital of CO.

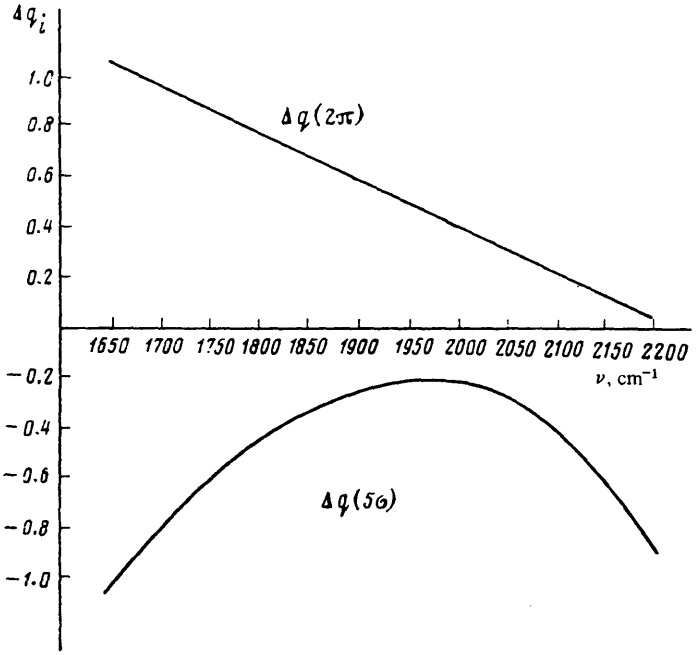



Figure 4. Dependence of the charge transfer $\Delta q(5\sigma)$ and $\Delta q(2\pi)$ to the CO molecule on its vibrational frequency in the coordinated state in the one-parameter two-level theory of vibronic activation on coordination. [23,24]

The relationship between $K'$ and $Q_0$ given above can be used to obtain a correlation diagram relating the vibration frequency of CO and the transfer of charge from the $5\sigma$ HOMO to the active centre ($-\Delta q_1$) and from the latter to the $2\pi$ LUMO ($\Delta q_2$) on coordination, [23,24] shown in Fig.4. It may be noted, however, that the empirical relationship $K' = f(Q_0)$ was obtained for the range where the charge transfer and the change in the CO vibration frequency are not too small. With allowance for the correlation between $K'$ and $Q_0$, the vibronic theory of activation becomes one-parameter, that is all the results depend on one parameter, namely the value of the vibration frequency of CO in the coordinated state (or $K'$).

In this approximation, the change in the reactivity of CO on the NiO surface, obtained from Eqn.(29), gives the following relationship (values of $D$ and $\Delta D$ in kcal mole$^{-1}$):

$$\Delta D = -0.17D - 1.40D^{1/4} + 0.78 - 0.15D^{-1/4} \cdot \qquad (36)$$

The $\Delta D = f(D)$ curve for this case, together with other analogous curves obtained for a number of coordination centres which activate CO, is given in Fig.5.[22]

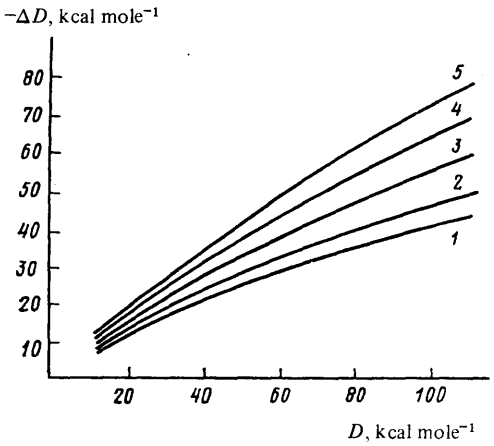



Figure 5. $\Delta D = f(D)$ relationships for the activation of the CO molecule on coordination to various systems, constructed from vibronic theory for the systems: *1*) Pd–Co, *2*) Ni–Co, *3*) $Fe(CO)_5$, *4*) $V(CO)_5$, *5*) $Mn(CO)_5$.

To estimate the efficiency of Eqn.(36) it is necessary to obtain the numerical values of $\Delta D$ for a known $D$ and to compare them with the experimental values. If it is assumed that the activation energy of the reaction $CO + O_2 \rightarrow CO_2 + O$ in a flame ($D$ = 48 kcal mole$^{-1}$)[29] corresponds to the activation of CO, then for linear coordination on a nickel oxide surface, according to Eqn.(36), the activation energy decreases by $\Delta D \cong -17$ kcal mole$^{-1}$ and becomes equal to $D' = D + \Delta D \cong 31$ kcal mole$^{-1}$, in good qualitative agreement with the experimental data for this reaction on a nickel catalyst, for which (in an excess of CO) $D_{expt}$ = 25.4 kcal mole$^{-1}$.[30]

Interesting results have been obtained in a study of the vibronic activation of CO on transition metal clusters.[23] It has been found, in particular, that CO molecules coordinated simultaneously to two (in $Co_2(CO)_8$) and more particularly to three (in $Rh_6(CO)_{16}$) metal atoms are activated to a much greater extent than when coordinated to one atom. On the other hand, in $Mn_2(CO)_{10}$ the axial CO groups are activated to a much greater extent than the equatorial groups.

The $N_2$ molecule, which is isoelectronic with CO, also has a $5\sigma$ HOMO and a $2\pi$ LUMO. The experimental data for $N_2^+$ and the excited states $a^1\Pi g$ and $B^3\Pi_g$[31] (the latter correspond to the excitation $5\sigma^2 \rightarrow 5\sigma^1 2\pi^1$ with $\Delta q_1 = -1$ and $\Delta q_2 = 1$) give from Eqns.(30)–(32) the following values for the vibronic parameters:[7–10]

$$\begin{aligned} f^{(1)} &= 3.51 \cdot 10^{-4} \text{ dyn} \\ k^{(1)} &= 0.286 \cdot 10^{6} \text{ dyn cm}^{-1} \\ C^{(1)} &= 0.112 \\ f^{(2)} &= -8{,}18 \cdot 10^{-11} \text{ dyn} \\ k^{(2)} &= -0{,}785 \cdot 10^{6} \text{ dyn cm}^{-1} \\ C^{(2)} &= 0.127 \end{aligned} \qquad (37)$$

It can be seen that the highest occupied $5\sigma$ orbital of the $N_2$ molecule, unlike that of CO, is bonding, but the $2\pi$ LUMO, as in CO, is antibonding. Thus in contrast to CO, for the activation of $N_2$ the coordination centre for longitudinal linear coordination should be a good $\pi$-acceptor and $\pi$-donor. In principle, an analogous effect brings about charge transfer to the coordination centre through the $\pi$-bond, which in the case of linear coordination may take place from the deeper-lying $\pi_u$ orbital. For transverse coordination this transfer can take place only from the antibonding $\sigma_u$ orbital. This explains the differences in the activation of $N_2$ with respect to the coordination geometry (see Refs.7–9 for more details). Estimates of the orbital vibronic constants are also given in Ref.32.

The Table gives examples of calculations of the changes in activation energy and charge transfer for a number of specific cases of the coordination of an $N_2$ molecule to transition metal complexes.[3,10] The vibrational frequencies of coordinated $N_2$ were taken from Ref.33, and the values of $Q_0$ were estimated from the empirical equation ($\nu'$ in cm$^{-1}$):

$$Q_0, \text{ Å} = 0.9482 - 0.7105(\nu' \cdot 10^{-3}) + 0.1302(\nu' \cdot 10^{-3})^2 \qquad (38)$$

The Table shows particularly, that as expected in the general case, the greatest contribution to $\Delta D$ on coordination is due to the linear vibronic effect, that is to the production of the deforming force (terms with coefficients $b$ and $c$ in Eqn.(34)), that the softening influence (the quadratic term with coefficient $a$) makes a smaller contribution, and that the anharmonicity terms (with coefficient $d$) make a very small contribution.

Semi-empirical estimates of the charge transfer to the HOMO $\Delta q_1$ and LUMO $\Delta q_2$ and the lowering of the activation energy $\Delta D = aD + bD^{1/2} + c + dD^{-1/2}$ of the $N_2$ molecule on coordination (one-parameter approximation).

| Coordination system | $\nu'$, cm$^{-1}$ | $10^{-6}K'$, dyn cm$^{-1}$ | $10^{-6}\Delta K$, dyn cm$^{-1}$ | $C_0$, Å | $10^4 F$, dyn | $\Delta q_1$ | $\Delta q_2$ | $a$ | $b$ | $c$ | $d$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $[RuH_2(N_2)(PPh)_3]$ | 2147 | 1.900 | −0.394 | 0.0229 | −4.19 | −0.16 | 0.44 | −0.14 | −2.72 | 2.87 | −0.01 |
| $[\{Ru(NH_3)_5\}_2N_2]^{4+}$ | 2100 | 1.821 | −0.479 | 0.0303 | −5.25 | −0.57 | 0.41 | −0.21 | −3.37 | 4.81 | −2.28 |
| $[Os(NH_3)_5N_2]Br_2$ | 2028 | 1.695 | −0.599 | 0.0428 | −6.77 | −1.00 | 0.40 | −0.31 | −4.32 | 8.94 | −6.17 |
| $[(tol)(PPh_3)_2Mo-N_2-Fe(C_5H_5)(dmpl)]^+$ | 1930 | 1.536 | −0.758 | 0.0619 | −8.54 | −1.21 | 0.52 | −0.37 | −5.62 | 16.9 | −17.0 |

Note: tol = toluene, dmpl = $Me_2PCH_2CH_2PMe_2$, $\Delta K = K' - K$.

Analogous estimates of the activation on coordination have been carried out for a number of other small molecules, including NO, $O_2$, $C_2H_4$, $C_3H_8$, etc.[3,10]

## V. ELECTRON-CONFORMATIONAL INTERACTIONS. APPLICATIONS TO METALLOPORPHYRINS AND HAEM-CONTAINING PROTEINS

In the previous section it was shown how a change in the electronic structure of a molecular system leads via vibronic coupling to the production of a force which deforms the core of the molecule in a definite direction, to a change in the force constant, which "softens" this system (or makes it "harder"), to a change in the anharmonicity constants, etc. These changes alter the form of the adiabatic potential, including its behaviour at large distances, that is the reactivity of the system. The change in reactivity has an influence, however, in the interaction of the given system with another system, with which it undergoes a chemical reaction. Under different conditions (in the absence of this interaction), other effects, resulting from the above changes in the parameters of the system, are more significant.

In particular, a direct result of the production of a non-zero deforming force

$$F_{\bar{\Gamma}} = \sum_i \Delta q_i f^i_{\bar{\Gamma}}$$

(Eqn.(24)) is a change in the spatial configuration (geometry) of the system in the direction $Q_{\bar{\Gamma}}$. The latter is determined by the symmetry of the molecular orbitals $i$, for which the orbital vibronic constant $f^i_{\bar{\Gamma}}$ and the changes in the populations $\Delta q_i$ are non-zero. The representations $\bar{\Gamma}$ for which $f^i_{\bar{\Gamma}}$ is non-zero, as already noted, are found directly. If the $i$th MO is non-degenerate, then $\bar{\Gamma} = \bar{\Gamma}_i \times \bar{\Gamma}_i = A_1$, that is the direction $Q_{\bar{\Gamma}}$ can only be totally symmetric. In other words, a change in the population of the non-degenerate molecular orbitals changes only the interatomic distances, without changing the symmetry of the system (without distorting it). If however the orbital state $\Gamma_i$ is degenerate, then $\bar{\Gamma} = [\Gamma_i \times \Gamma_i]$ contains both totally symmetric and non-totally-symmetric representations, so that the presence of electrons in these orbitals leads to distortion of the system; the direction of the distortion coincides with the direction of the distortion in the Jahn–Teller effect.[2]

If the change in the electronic structure changes the populations $\Delta q_i$ of not one but several MO, and the directions of the deformation of the core, determined by the coordinate $Q_{\bar{\Gamma}}$, are different for these orbitals, then the total distortion will be equal to their vector sum. To determine the latter it is also necessary to know the magnitude of the distortion $Q_{0\bar{\Gamma}}$ in each of the directions $Q_{\bar{\Gamma}}$. In the approximation linear with respect to the vibronic interaction, it is determined directly from the relationship

$$Q_{0\bar{\Gamma}} = F_{\bar{\Gamma}}/K_{\bar{\Gamma}} \qquad (39)$$

where $K_{\bar{\Gamma}}$ is the force constant in the direction $Q_{\bar{\Gamma}}$. With allowance for the change in the latter and the anharmonicity constant as a result of the change in the electronic structure, the expression for $Q_{0\bar{\Gamma}}$ becomes more complex, and takes the form given in Eqns.(27). Substituting the expression for $F_{\bar{\Gamma}}$ in Eqn.(39) gives

$$Q_{0\bar{\Gamma}} = \sum_i \Delta q_i f^i_{\bar{\Gamma}}/K_{\bar{\Gamma}} \ . \qquad (40)$$

From this it can be seen that in the directions $Q_{\bar{\Gamma}}$ for which $f^i_{\bar{\Gamma}}$ is small and the hardness of the molecule is high ($K_{\bar{\Gamma}}$ large), $Q_{0\Gamma}$ is small. In other words, a contribution to the distortion of the molecule in the given direction is made only by those orbitals for which the vibronic constant is sufficiently high, which is the case when the orbital being considered is sufficiently effectively involved in the bonding (antibonding) system in the given direction. On the other hand, appreciable distortions may take place in those directions in which the system is sufficiently "soft" (that is $K_{\bar{\Gamma}}$ is small). Similarly, Eqn.(25) makes it possible to estimate the softening or hardening (in the sense of the change in the force constant and the vibrational frequency) of the system in the direction $Q_{\bar{\Gamma}}$.

In simple cases these effects are qualitatively completely understandable from general considerations, but the above equations give quantitative estimates for these effects in the general case, and make it possible to predict them.

The change in the configuration of a molecule and its hardness with change in its electronic structure is directly related to the so-called electron-conformational interactions. The latter essentially coincide with the vibronic interactions, and the apparatus developed above can be used directly to analyse electron-conformational effects. Most frequently, electron-conformational transitions in which the appearance or disappearance of one electron leads to a change in the conformation of the system are considered. In this formulation, the problem is solved approximately using the above scheme, in which the additional population of the $i$th orbital ($\Delta q_i = 1$) with $f^i_{\bar{\Gamma}} \neq 0$ leads to fairly strong distortion of the system in the direction $Q_{\bar{\Gamma}}$, particularly if the value of $K_{\bar{\Gamma}}$ in this direction is small. For large systems, the appearance of an electron in a given position, usually in the active centre, leads to a local distortion $Q_{0\bar{\Gamma}}$ which initiates a conformational transformation of the system as a whole (the so-called trigger mechanism).

The electron-conformational transitions in biological systems are of particular interest. For example, in haemoglobin the displacement of the iron atom from the haem plane in the deoxy-form and its return on oxygenation, according to Perutz,[34,35] initiates a conformational $T \rightarrow R$ transition. This transition is determined by the cooperative properties of the four active iron centres in haemoglobin, and leads to the unusual $S$-shaped kinetic curve for the oxygenation (the "trigger" mechanism of the oxygenation of haemoglobin). The analogous haem-centres in various proteins have a wide range of functions, from electron transfer to the oxidation of saturated hydrocarbons, and all of these functions are related in some form or other to electron-conformational interactions. As noted above, the distortions of the molecular system due to electron rearrangement (Eqn.(40)), like the Jahn–Teller effect and pseudo-effect, are greater, the softer the system (that is the smaller $K_{\bar{\Gamma}}$) in the direction $Q_{\bar{\Gamma}}$ being considered.

A distinguishing feature of biological systems is that, because of the large number of atoms present, there are soft modes which give the vibronic effects a high efficiency. On the other hand, because of the large dimensions, the initial ("trigger") electron rearrangement generally takes place locally in an active centre, initiating the conformational transition of the system as a whole.

The electron-conformational and other vibronic effects in metalloporphyrins and haem-containing proteins[36–43] can be considered as examples illustrating these ideas. In addition to their independent interest for biology, these examples are of general importance, since the behaviour of the active

centre in them reflects the general situation arising in many coordination and organometallic compounds similar to metalloporphyrins. A distinguishing feature of these systems is the presence of close energy levels of the *d* electrons of the metal and the π-system of the porphyrin ring (or other similar ligands). If for example (as in metalloporphyrins) these states mix as a result of nuclear displacements of type $A_{2u}$, which move the metal atom from the plane of the porphyrin ring (Fig.6), then when it is sufficiently strong, this vibronic mixing softens the system or even makes it unstable with respect to this displacement of the metal from the plane (Jahn–Teller pseudo-effect). The explanation for the displacement of the metal atom from the plane of the porphyrin ring is that this displacement leads to the formation of additional metal–ligand π-bonds (for the metal atom situated in the plane of the porphyrin ring, the overlap of the corresponding orbitals is equal to zero), whose contribution to the bond energy is greater than the decrease in the strength of the corresponding σ-bonds.

As a result of the Jahn–Teller pseudo-effect, the force constant $K$ for displacements in the direction $Q$, as noted above, decreases by $F^2/\Delta$, where $F = \langle 1|(\partial V/\partial Q)_0|2\rangle$ is the corresponding vibronic constant; if $(F^2/\Delta) > K$, the system becomes unstable with respect to $Q$-displacements. For the metalloporphyrins with $D_{4h}$ symmetry being considered, the $Q$-displacement of the metal atom from the plane of the porphyrin ring relates to the $A_{2u}$ representation (Fig.6). This means that in order to have $F \neq 0$, the product of the representations of the mixing states 1 and 2 must contain the representation $A_{2u}$.

Fig.7 gives the highest occupied and lowest unoccupied energy levels of the molecular orbitals of a number of metalloporphyrins of Mn, Fe, Co, Ni, Cu and Zn, and (for comparison) manganese phthalocyanine (MnPc), obtained from a calculation for the planar configuration.[44,45] Figs.5 and 6 show that, for example, for FeP the ground state is $^3E_g$, so that the excited state, which is displaced with it for $A_{2u}$ displacements, should have $^3E_u$ symmetry ($E_g \times A_{2u} = E_u$); for MnP, MnPc, and CoP, the corresponding excited states are $^4A_{2g}$, $^4E_g$, and $^2A_{2u}$. They can all be obtained by one-electron excitation from the $a_{2u}(\pi)$-level of (mainly) the porphyrin ring into the unoccupied $a_{1g}(d_{z^2})$-level of (mainly) the metal; here, $2\Delta \cong \varepsilon(a_{1g}) - \varepsilon(a_{2u})$ is comparatively small. For other metalloporphyrins, NiP, CuP, and ZnP, this $a_{1g}$ orbital is occupied by electrons (Fig.7), and the next MO with the same symmetry are very high above it (not shown in Fig.7). Thus the last three metalloporphyrins show practically no Jahn–Teller pseudo-effect with respect to displacement of the metal atom from the plane, whereas the effect can appear in other systems.

To estimate this possibility, it may be noted that the calculated values of $2\Delta$ in the series MnP, FeP, CoP, and MnPC are 0.15, 0.2, 0.6, and 1.0 eV respectively.[44,45] The vibronic constant estimated[38] for FeP is $F \cong 10^{-4}$ dyn (for other metalloporphyrins, calculations for the same states give values of $F$ of the same order of magnitude), and the force constant of the $A_{2u}$ displacement is $K \cong 10^4$ dyn cm$^{-1}$ Thus $(F^2/K) \cong 0.1$ eV, that is $F^2/K$ and $\Delta$ are of the same order of magnitude, so that the ground state is softened considerably as a result of the Jahn–Teller pseudo-effect. The porphyrins MnP and FeP ($\Delta \cong 0.08$ eV and 0.1 eV) may be unstable, since for them $\Delta < F^2/K$, whereas for CoP and MnPc ($\Delta \cong 0.3$ and 0.5), the position of the metal is softened, although it is stable. These results are in complete qualitative agreement with experimental data.[46,47]

Thus the observed displacement of the iron atom from the plane in the deoxy-form of haemoglobin (and in other analogous systems) is satisfactorily explained in terms of the Jahn–Teller pseudo-effect (the existence of a bond with the imidazole residue (Fig.6) does not lead to qualitative changes, since the energy levels $a_{1g}$ and $a_{2u}$ do not move apart to a significant extent;[48] see Refs.41–43 for more details). It is of interest to explain from the same viewpoint the return of the iron atom to the haem plane on oxygenation, initiating the above-mentioned conformational $T \rightarrow R$ transition. Fig.8 gives the MO energy levels for planar FeP, the deoxy-form of haemoglobin (Hb), and the changes in these levels when $O_2$ and CO are coordinated.[44,48] It can be seen that the comparatively small difference $2\Delta = \varepsilon(a_{1g}) - \varepsilon(a_{2u})$, which ensures softening and instability in the first two systems, including the deoxy-form of haemoglobin, increases sharply when $O_2$ or CO are added ($2\Delta \cong 3$ eV for $HbO_2$ and $2\Delta \cong 4$ eV

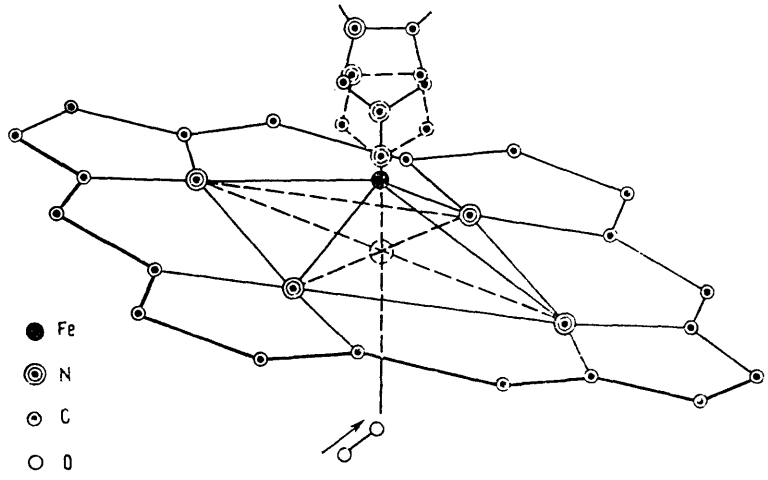



**Figure 6.** The structure of metalloporphyrins and the corresponding fragments of haem-containing proteins. The two positions of the iron atom together with the imidazole group of histidine correspond to the deoxy-form (continuous lines) and the oxygenated configuration (broken lines).

for HbCO). The increase in $\Delta$ removes completely the Jahn–Teller pseudo-effect, and the position of the iron atom becomes stable in the haem plane; this leads to the above-mentioned $T \rightarrow R$ conformational transition in the system (the trigger mechanism of the oxygenation of haemoglobin). At the same time, the increase in $\Delta$ may (and does, see Fig. 8) lead to a change in the spin state from $S = 2$ to $S = 0$, which is extremely typical of the compounds of iron and various other transition metals, and is known as "cross-over" (the conversion of the high-spin to the low-spin state takes place when $\Delta > \Pi$, where $\Pi$ is the binding energy of the electrons in the corresponding orbitals.[1] This question is examined in more detail in Refs. 41–43.

It may be noted that since the geometry and multiplicity of metalloporphyrins depends on the interaction of the $a_{2u}(\pi)$-orbital, which is sensitive to the introduction of substituents at the periphery of the ring, with the $a_{1g}(d_{z^2})$ orbital, which is affected by the axial ligands of the metalloporphyrin, the properties of these systems may depend markedly on the protein environment in haem proteins, as in fact observed.

It has been found that not only the displacement of the metal from the plane and its return with change in the electronic structure, but also the geometry of the coordination of small ligands (NO, $O_2$, CO, etc.) and the unusual quantum yield of photolysis, which depends markedly on this geometry, are explained by vibronic effects, critically dependent on the electronic structure.[39–43] Overall, the approach is of course general in character and can be applied to any molecular formations in chemistry and biology.[3]

The chemical aspects of the concept of vibronic interactions examined above make it possible to reach a number of conclusions of general importance for present-day chemistry. The concept of vibronic interactions involves taking more detailed account (compared with the adiabatic approximation) of the effect of the electrons on the nuclear configuration and its dynamics, resulting from the vibronic mixing of the electronic states by the nuclear displacements. The orbital vibronic constants introduced provide a new and more complete (extended into the dynamic range) description of the electronic structure of molecules in the molecular orbital approximation. The new description makes it possible to predict changes in the nuclear configuration and its dynamics with change (perturbation) in the electronic structure.

It follows from vibronic theory that the only source of dynamic instability in molecular systems is the vibronic mixing of the ground state with one (or possibly several) excited states. This conclusion opens up extensive possibilities for explaining and predicting the stereochemistry and crystal chemistry of chemical compounds, and also for analysing the origin and studying the intermediate states of chemical reactions.

It has been shown that vibronic effects lead to a lowering of the barriers to reaction with other molecules in definite directions, that is to an increase in reactivity for certain reaction mechanisms. The knowledge of the mechanism for the production of instability and reactivity has been used to develop a theory of the process by which reactivity is induced under the influence of another molecular system, that is the theory of chemical activation on coordination. The

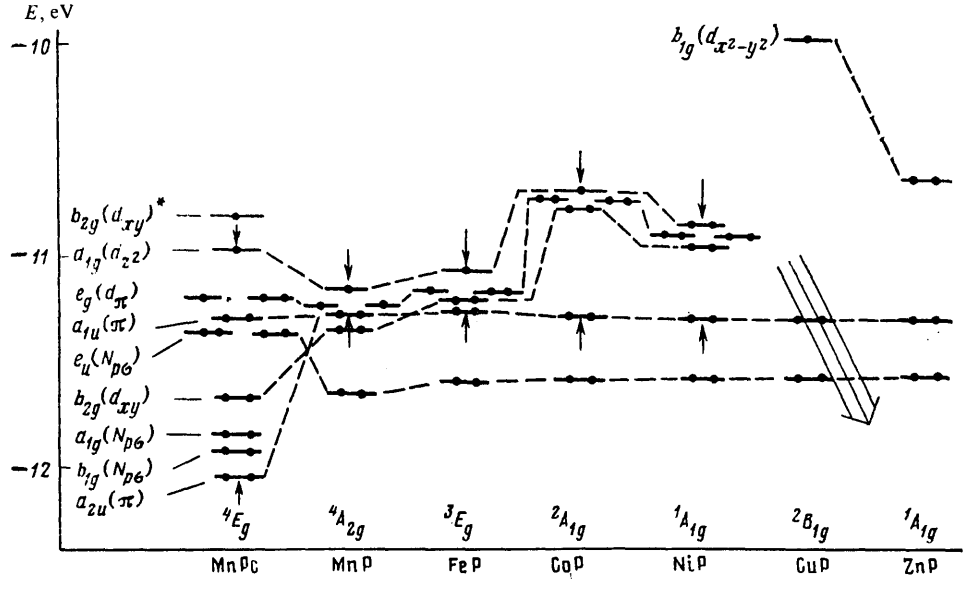



Figure 7. Energy levels of some HOMO and LUMO for metalloporphyrins and manganese phthalocyanine (MnPc); the ground terms of the systems in the configuration with the metal in the plane of the porphyrin (phthalocyanine) ring are indicated. The arrows indicate the energy gaps $2\Delta$ between the ground and lowest excited states, which are mixed in the $A_{2u}$ displacements of the metal.

orbital vibronic constants have been used to develop a semi-empirical two-level version of the theory, which makes possible an approximate prediction of chemical activation (lowering the activation energy of the reaction) on coordination to a given catalyst active centre.

In addition, vibronic effects form the basis of electron-conformational transformations in chemistry and biology, as has been demonstrated for specific examples, namely metalloporphyrins and haem-containing proteins.

Each of these conclusions (except the first) requires further development in detail, and the applied aspects, with some development, may each become a starting point for a new direction in this field of study. This confirms the conceptual character of the new approach to the structure–property problem briefly presented in the present review.

In general, as already noted, the concept of the mixing of electronic states as a result of nuclear displacements (produced by abandoning the separate description of the movements of the electrons and the nuclei in the simple adiabatic approximation) introduces new elements into the chemist's way of thinking, making it possible to avoid restricting stereotypes. In the new understanding, in particular, the ground and excited states of a molecule for a given configuration of the nuclei, strictly speaking, no

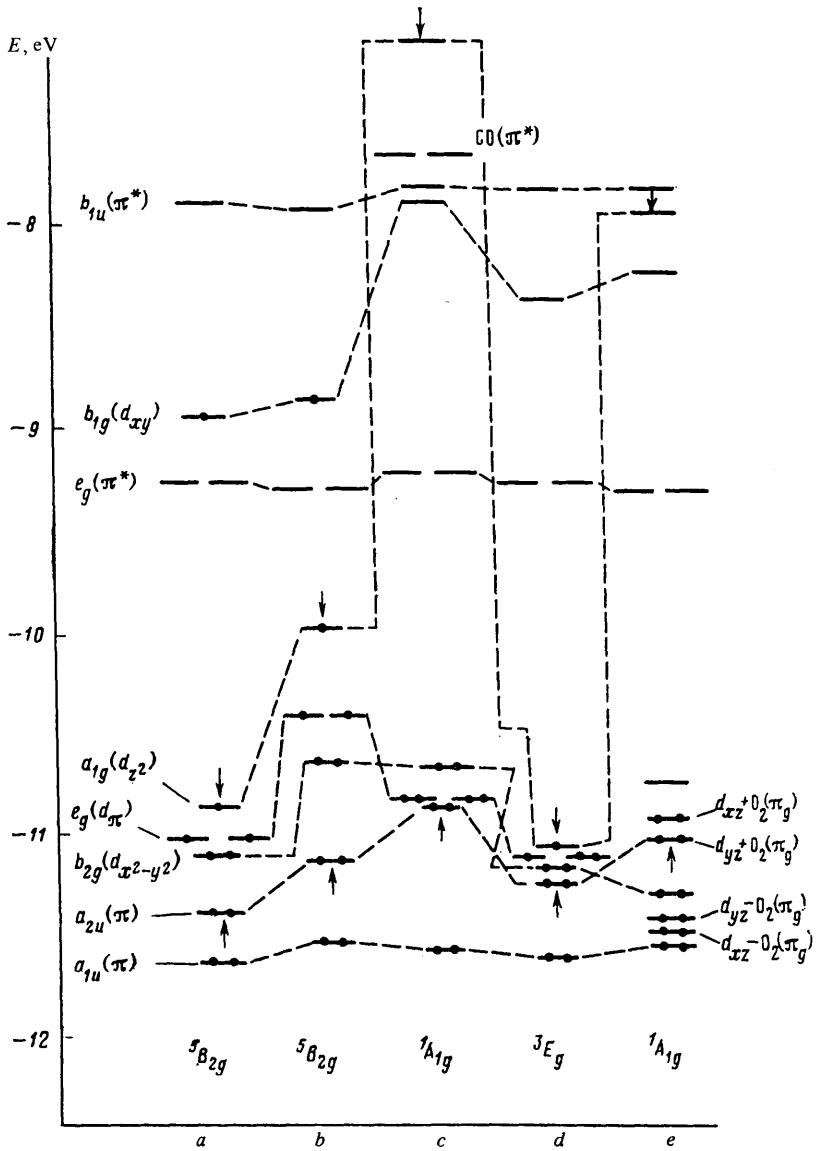



**Figure 8.** Energy levels of some HOMO and LUMO: *a*) FeP in the configuration with the Fe atom displaced from the porphyrin plane by $\Delta R = 0.49$ Å; *b*) the deoxy-form of haemoglobin with $\Delta R = 0.62$ Å; *c*) Hb–CO system; *d*) planar FeP, that is $\Delta R = 0$; *e*) Hb–$O_2$ system. The ground term and (arrows) the gap $2\Delta$ between the states mixed in the displacement of the iron atom from the plane of the porphyrin ring are indicated.

longer exist as independent concepts; they may be mixed considerably when allowance is made for the displacements of the nuclei. In other words, the excited electronic states of the molecular configuration being considered may determine its properties in the ground state to the same extent as the ground electronic state in this configuration.

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# The Preparation and Properties of Indium Phosphide

V.P.Talyzin and A.Ya.Nashel'skii

The present review examines recent work on the synthesis of polycrystalline specimens of indium phosphide and the growth of single crystals of this compound for the modern electronics industry. The synthesis of polycrystalline indium phosphide by different methods is examined. Particular attention has been paid to work on the preparation of highly pure material and the growth of single crystals with a low concentration of dislocations and single crystals oriented along ⟨100⟩.
The bibliography contains 45 references.

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## I. INTRODUCTION

In recent years, in the development of work in optoelectronics (the use of optical and electronic effects in semiconductors to create instruments and information systems of fundamentally new types) and SHF (super-high-frequency) technology, there has been a marked increase in interest in single crystals of indium phosphide. Indium phosphide now occupies third place in the world after silicon and gallium arsenide in importance for application in special instruments. Non-doped single crystals of indium phosphide are used as supports in the manufacture of instruments in SHF technology. The main requirement in this material is a low concentration of impurities, which affect the parameters of the instruments, and a low density of dislocations. Field transistors are produced on supports of single crystals of semi-insulating indium phosphide with a high specific resistance ($\rho > 10^7$ Ω.cm). The main application of single crystals of indium phosphide, however, is in optoelectronics, for producing radiation sources and receivers operating in the wavelength range 1.0–1.6 μm.

## II. THE PREPARATION OF HIGHLY PURE INDIUM PHOSPHIDE CRYSTALS

Non-doped polycrystalline indium phosphide is obtained chiefly by the following methods: horizontal directed crystallisation, horizontal zone fusion, crystallisation of melts with non-stoichiometric composition in a temperature gradient (so-called "synthesis with diffusion through a melt"), and synthesis in quasi-hermetic reactors. Polycrystalline indium phosphide is used in liquid-phase epitaxy and as starting material for growing single crystals.

### 1. Horizontal Directed Crystallisation (HDC)

The synthesis of indium phosphide by HDC has been carried out in an autoclave.[1,2] Boats of pyrolytic boron nitride (PBN) or quartz containing indium and red phosphorus were placed in a sealed quartz ampoule (reactor). The synthesis was carried out at the melting point of the indium–indium phosphide melt (1070 °C) at the equilibrium vapour pressure of phosphorus, 27.5 atm (the temperature of the section of the ampoule containing phosphorus was ~600 °C). The boat containing indium was heated at a rate of 20–35 K $h^{-1}$, and that containing phosphorus at a rate of 10 K $h^{-1}$. The pressure of inert gas in the autoclave was raised simultaneously. The low heating rates prevented rupture of the ampoule with increase in the phosphorus vapour pressure. When the reaction was complete, the temperature of the hot zone (the zone containing the indium–indium phosphide melt) was lowered at a rate ensuring crystallisation (0.2–0.5 cm $h^{-1}$). Indium phosphide ingots with a mass of 110 g were obtained after 170 h.[2] The concentration of principal current carriers in these ingots was $n = (2–5) \times 10^{15}$ $cm^{-3}$ (300 K).

HDC has been used[3] to obtain polycrystalline indium phosphide ingots with a mass of 1100 g. The synthesis was carried out in an autoclave, in a quartz ampoule with diameter 34–38 mm and length 300 mm. This gave a product with $n = (5–50) \times 10^{15}$ $cm^{-3}$ and a mobility of principal charge carriers $u = (1.5–2.5) \times 10^4$ $cm^2$ $V^{-1}$ $s^{-1}$ (77 K). The concentration of silicon did not exceed $(2–3) \times 10^{-5}$ at.% or $(4–6) \times 10^{15}$ atom $cm^{-3}$. The authors cited consider that the main source of silicon in the indium phosphide is impurities in the original indium.

In Ref.4, the purity of indium phosphide was increased by heating the indium at 700 °C successively (100 h) in a stream of moist hydrogen and in a vacuum at $10^{-7}$ mmHg, and heating the phosphorus in a vacuum at 300–335 °C for 24 h. The quartz parts of the reaction vessel, after etching, were heated in a vacuum at 1000 °C before assembling the reaction vessel. The PBN boats were also specially treated. Under these conditions, ingots of polycrystalline indium phosphide with $n = 10^{15}$ $cm^{-3}$ and $u = (3–4) \times 10^4$ $cm^2$ $V^{-1}$ $s^{-1}$ (77 K) were obtained.

A significant increase in the purity of polycrystalline indium phosphide is achieved by recrystallising its non-stoichiometric melts. In Ref.5, indium phosphide synthesised at the equilibrium vapour pressure of phosphorus had $n = 3.50 \times 10^{15}$ $cm^{-3}$ and $u = 2.52 \times 10^4$ $cm^2$ $V^{-1}$ $s^{-1}$ (77 K), whereas the material obtained at a lower phosphorus vapour pressure above the melt (lower than 10 atm) had $n = 3.16 \times 10^{15}$ $cm^{-3}$ and $u = 3.89 \times 10^4$ $cm^2$ $V^{-1}$ $s^{-1}$. The crystallisation of melts with non-stoichiometric composition, however, requires a decrease in the crystallisation rate (12 mm $d^{-1}$).

To increase the purity of indium phosphide synthesised by HDC, indium(III) oxide was added to the reaction vessel to an atomic fraction of $10^{-4}$–$10^{-5}$. The doping with oxygen was carried out for two sets of growth conditions, with one high-temperature zone (1080 °C) in an ampoule with length 100 mm, and with two zones (1080 °C and 630 °C) in an ampoule of length 300 mm.[6]

Measurement of the electrical parameters by the Hall effect method showed a decrease in the concentration of charge carriers and an increase in their mobility compared with specimens not doped with oxygen only when the doped indium phosphide was grown in a single temperature zone: the values were $(1.5–7) \times 10^{15}$ cm$^{-3}$ and $(2–3.3) \times 10^{4}$ cm$^2$ V$^{-1}$ s$^{-1}$ (77 K) respectively. The influence of oxygen under these conditions is due to the decrease in the concentration of the silicon fine donor impurity in the indium phosphide crystal.

To increase the productivity of the synthesis of indium phosphide by HDC and to prevent possible rupture of the sealed quartz reactors, they are fitted with a quartz bellows, which connects the quartz rod to the pressure measuring device in the autoclave.[7] The signal from the measuring device is passed to a system which equalises the pressure in the reactor and the autoclave (Fig.1). In an autoclave fitted with this system it is possible to synthesise in 1 h 2 kg of indium phosphide with parameters $n = 1.5 \times 10^{16}$ cm$^{-3}$ and $u = 1.5 \times 10^{4}$ cm$^2$ V$^{-1}$ s$^{-1}$ (77 K).

In work at one of the leading firms producing semiconducting compounds, Metal Chemical Products (England),[8] the pressure in the ampoule and in the autoclave is controlled using a quartz reaction vessel, in the end face of which there is sealed a corrugated quartz diaphragm, connecting the rod to the pressure measuring device. The signal from the measuring device operates solenoid valves to supply gas to the autoclave or to release the pressure when the phosphorus vapour pressure in the reactor increases. This system gives a differential pressure difference of 0.25–0.5 atm, depending on the sensitivity of the diaphragm.

The conditions for obtaining ingots of indium phosphide with improved parameters were investigated in the same study: the main requirement was additional treatment of the starting materials. Indium was heated in a vacuum at 900 °C (12 h). The time taken to synthesise a melt with a mass of 2 kg in quartz boats at a phosphorus vapour pressure of 24.5–30 atm was 20 h, and the crystallisation rate was 10–20 mm h$^{-1}$. The polycrystalline indium phosphide ingots obtained under these conditions had $n = 5 \times 10^{5}$ cm$^{-3}$ and $u = (2–4) \times 10^{4}$ cm$^2$ V$^{-1}$ s$^{-1}$ (77 K); the silicon concentration was $2 \times 10^{-5}$ mass % or $2 \times 10^{15}$ atom cm$^{-3}$.

## 2. Horizontal Zone Fusion (HZF)

The HZF directed crystallisation method is widely used by Western European firms to obtain polycrystalline highly pure indium phosphide. The product has been synthesised in an autoclave, in a sealed quartz ampoule.[9,10] The temperature of the molten zone was 1100 °C, and the phosphorus vapour pressure 27.5 atm. The ampoule was moved relative to the inductor at a rate of 6 cm h$^{-1}$, and after 6 h, 1.3 kg of polycrystalline indium phosphide was obtained:[10] $n = (5–10) \times 10^{15}$ cm$^{-3}$, $u = 3700–4700$ cm$^2$ V$^{-1}$ s$^{-1}$ (300 K). The concentration of silicon in the indium phosphide ingots obtained did not exceed $10^{16}$ atm cm$^{-3}$. The main source of silicon in the product was the impurities in the original indium.

With increase in the temperature of the molten zone from 1050 °C to 1180 °C, the concentration of principal charge carriers increased approximately 100-fold, due to an increase in the silicon concentration.[11] The authors cited point out that decrease in the phosphorus vapour pressure in the ampoule to 2 atm makes possible an approximately five-fold decrease in the concentration of principal charge carriers. To increase the purity of the polycrystalline specimens obtained, the original indium was heated beforehand in a vacuum (3 h) at 450–950 °C. The temperature conditions of the preliminary vacuum treatment of the original indium had the greatest influence on the purity of the synthesised indium phosphide. In the opinion of the authors cited, the concentration of silicon in polycrystalline indium phosphide is lower if the original metallic indium contains oxides, which decompose in a vacuum at >800 °C. Increase in the indium heating temperature from 700 °C to 800 °C led to a sharp increase in the concentration of both the principal charge

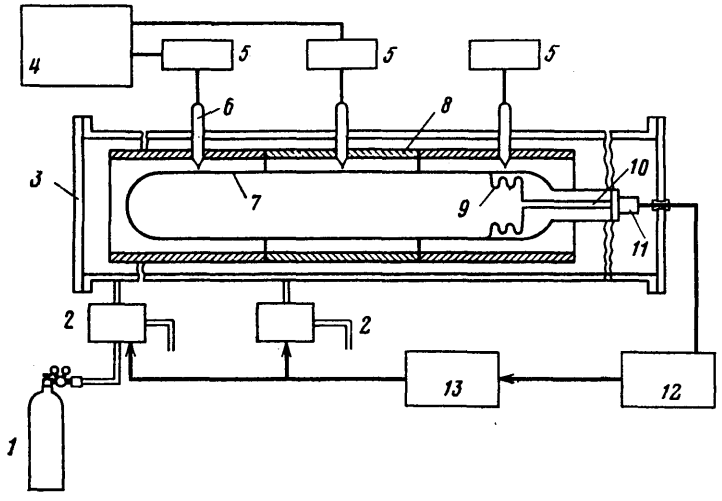



**Figure 1.** Block diagram of the high-pressure apparatus for synthesising polycrystalline indium phosphide ingots, fitted with a system balancing the pressure in the reactor and the autoclave: *1*) cyclinder of inert gas, *2*) high-pressure valve, with electric drive, *3*) autoclave, *4*) potentiometer, *5*) blocks of high-precision temperature regulators (HTR), *6*) thermocouple, *7*) reactor containing boat with indium and red phosphorus (not shown in the diagram), *8*) heater, *9*) quartz bellows, *10*) rod, *11*) high-pressure measuring device, *12*) amplifier, *13*) automatic regulator controlling the operation of the high-pressure valve.[7]

carriers and silicon in the polycrystalline indium phosphide obtained. The authors cited consider that the reaction of indium oxides with phosphorus vapour gives phosphorus(V) oxide, whose partial pressure in the ampoule increases, and the equilibrium[12]

$$10SiO_2(solid) + P_4(gas) \rightleftarrows 10SiO(gas) + P_4O_{10}(gas)$$

is displaced to the left, leading to contamination of indium phosphide by silicon from the quartz boat. Highly pure polycrystalline indium phosphide with $n = 3.2 \times 10^{15}$ cm$^{-3}$ and $u = 3.7 \times 10^4$ cm$^2$ V$^{-1}$ s$^{-1}$ (77 K) has been obtained.[11]

### 3. Crystallisation of a Melt with Non-stoichiometric Composition in a Temperature Gradient

This method of synthesising indium phosphide, called "synthesis with diffusion through a melt", is used mainly by Japanese firms. Recently, however, it has attracted interest from Western European research workers. The chief advantages are the simplicity of the equipment, which does not require the use of autoclave assemblies, and the high purity, compared with HDC and HZF, of the material obtained, resulting from the use of low synthesis temperatures (750–910 °C).

In Ref.13, indium phosphide was synthesised in a sealed quartz ampoule, placed in a two-zone furnace. The starting materials were red phosphorus (5 g) and indium (37.5 g), heated beforehand in a stream of hydrogen at 850 °C for 72 h. A quartz crucible containing red phosphorus was placed in the upper part of the ampoule, and indium in the lower part. The synthesis was carried out at 850 °C and a phosphorus vapour pressure of 0.8 atm (temperature of the upper part of the ampoule 400 °C). The temperature gradient required to crystallise indium phosphide from the saturated solution was created along the height of the melt. Under these conditions the synthesis was continued for 10 d to give a single-crystal ingot of indium phosphide with length and diameter 15 mm, mass 5.5 g, density of dislocations $N_d = 10^2$ cm$^{-2}$. When the process was complete, the indium was found to contain thin plates of indium phosphide with dimensions of several millimetres. The growth rate was 0.15 cm d$^{-1}$. The indium phosphide obtained under these conditions had $n = 2.3 \times 10^{14}$ cm$^{-3}$ and $u = 5.02 \times 10^4$ cm$^2$ V$^{-1}$ s$^{-1}$ (77 K).

To increase the purity of the product, indium was heated beforehand at 900 °C for 6 h; the red phosphorus was also heated beforehand (120 °C for 6 h). At a melt temperature of 910 °C and a temperature gradient in the melt of 20 K cm$^{-1}$, the indium phosphide obtained had $n = 6.4 \times 10^{14}$ cm$^{-3}$ (300 K) and $u = 7.91 \times 10^4$ cm$^2$ V$^{-1}$ s$^{-1}$ (77 K).[14] Later, the same authors reported the preparation of indium phosphide with $n = 5.9 \times 10^{14}$ cm$^{-3}$ (300 K) and $u = 9.67 \times 10^4$ cm$^2$ V$^{-1}$ s$^{-1}$.[15] The principal donor impurities in the indium phosphide are silicon and sulphur.

### 4. Synthesis of Indium Phosphide in Quasi-hermetic Reactors

The most productive method of obtaining polycrystalline indium phosphide is by synthesis in quasi-hermetic reactors, in an autoclave assembly. Fig.2 gives a diagram of the apparatus for synthesising polycrystalline indium phosphide ingots.[16] A hydraulic seal was used to connect the separate parts of the reactor, that is the quartz part containing red phosphorus and the graphite part containing the quartz crucible with indium.

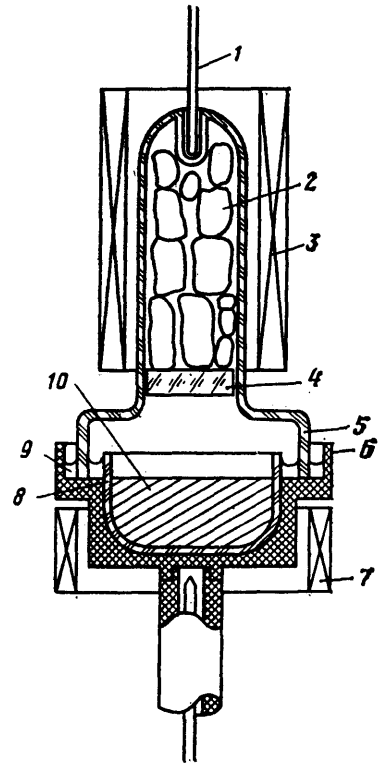



**Figure 2.** Diagram of the quasi-hermetic apparatus for synthesising indium phosphide by the reaction of phosphorus vapour with molten indium: *1*) thermocouple, *2*) phosphorus, *3*) electrical resistance heater, *4*) quartz plate, *5*) quartz reactor, *6*) graphite support, *7*) crucible heater, *8*) quartz crucible, *9*) channel of hydraulic seal, filled with indium, *10*) molten indium.[16]

A weighed specimen of indium (from one to several kilograms) was placed in the crucible. The corresponding stoichiometric quantity of red phosphorus, together with the calculated excess to fill the free volume of the reactor and to compensate the loss through the hydraulic seal (several percent of the total quantity) was placed in the quartz part of the reactor. The high-pressure chamber was evacuated, and then filled with an inert gas at a pressure such that after the heater was switched on, the working pressure in it was 60 to 70 atm. The red phosphorus was then heated to a temperature ensuring that the phosphorus vapour pressure created in the reactor was greater than the equilibrium vapour pressure over the molten compound with the stoichiometric composition (25 atm), and the crucible with the molten indium was heated to 1060 °C, and kept until the synthesis was complete. The temperature of the melt in the crucible was then lowered slowly to give a polycrystalline ingot of the compound. The material had electron conductivity and $n = (1–2) \times 10^{16}$ cm$^{-3}$ and $u = 3500–4500$ cm$^2$ V$^{-1}$ s$^{-1}$ (300 K).[16]

The time required to carry out the synthesis in a quasi-hermetic reactor by the HZF and HDC methods was calculated from the Nernst equation:[17]

$$\tau = \frac{-2.303 \cdot V \cdot \lg[(C_e - C_\tau)/(C_e - C_0)]}{F \cdot \alpha}$$

where $\alpha$ is the reaction coefficient (the rate constant of the first-order reaction taking place on the melt surface), cm $s^{-1}$; $F$ the surface area of the melt, $cm^2$; $C_e$ and $C_0$ the equilibrium (for the given temperature of the melt and vapour pressure of the volatile component) and initial concentrations of the volatile element in the melt, g $cm^{-3}$ or atom $cm^{-3}$; $V$ the volume of the molten non-volatile element, $cm^3$; and $C_\tau$ the concentration of the volatile element in the melt at moment of time $\tau$, g $cm^{-3}$ or atom $cm^{-3}$.

Fairly full thermochemical parameters of the synthesis of indium phosphide are given in Ref.18.

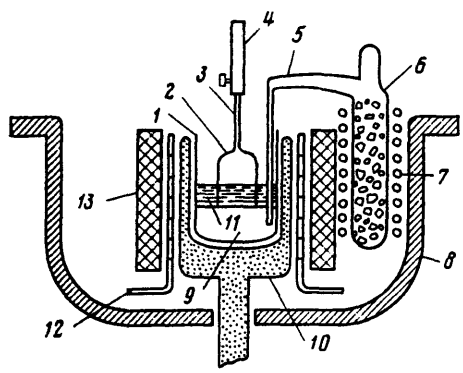



**Figure 3.** Diagram of the thermal unit of the high-pressure apparatus for obtaining indium phosphide crystals by the combined method (synthesis followed by crystal growth): *1*) crucible, *2*) crystal, *3*) seed, *4*) seed holder, *5*) tube for supplying phosphorus vapour from the reservoir, *6*,*7*) electrical resistance heater, *8*) autoclave body, *9*) melt, *10*) graphite support, *11*) layer of flux ($B_2O_3$), *12*) graphite electrical heater, *13*) heat reflecting screen.[19]

### 5. Combined Process

To increase the purity of polycrystalline and single-crystal indium phosphide, a combined process has been used: the synthesis was carried out directly in the apparatus used to grow single crystals; phosphorus vapour (30.6 atm) was supplied to molten indium under a layer of molten boric oxide (Fig.3).[19] The synthesis was carried out at the temperature of the indium–indium phosphide melt (1100 °C) for 1.5 h. This gave indium phosphide crystals with $n = (1.85–2.57) \times 10^{15}$ $cm^{-3}$ and $u = (3.03–3.18) \times 10^4$ $cm^2$ $V^{-1}$ $s^{-1}$ (77 K). The parameters of indium phosphide crystals obtained in quartz and PBN crucibles, and the silicon concentrations [$(0.3–0.5) \times 10^{-4}$ mass % or $(6–10) \times 10^{15}$ atom $cm^{-3}$], differed little. Approximately the same quantity of silicon is present in polycrystalline indium phosphide synthesised by other methods.

Examination of the methods for synthesising polycrystalline indium phosphide leads to the following conclusions.

1. To obtain weakly-doped single crystals with a concentration of charge carriers lower than $10^{17}$ $cm^{-3}$, the most suitable method is horizontal zone fusion. When systems controlling the pressure in the hermetic reactor and the gas pressure in the autoclave are developed, this method will satisfy all the requirements of ecological purity and safe operation.
2. Material to be used to grow highly-doped indium phosphide single crystals is best synthesised in a quasi-hermetic reactor. This method has a high productivity, and the cost of the final product is low.
3. The liquid-phase epitaxy of layers of indium phosphide and solid solutions based on it requires a relatively small quantity of highly pure polycrystalline indium phosphide. This material can be obtained by different versions of the directed crystallisation of indium–phosphorus melts with non-stoichiometric composition. Crystallisation at temperatures not exceeding 900 °C ensures minimum contamination of the final product by the reaction of the melt with the material of the container.

## III. THE GROWTH OF SINGLE CRYSTALS OF INDIUM PHOSPHIDE BY LIQUID HERMETIC SEALING OF THE MELT

### 1. Apparatus and Conditions for Growing Single Crystals of Indium Phosphide without Twins

One of the most widely encountered versions of the Czochralski method[18] is the so-called method of liquid hermetic sealing of the melt with a flux (LHM), widely used to grow single crystals of semiconducting compounds which may decompose. Single crystals of indium phosphide are grown by LHM in autoclave assemblies using resistance or high-frequency heating. The process is carried out in an inert gas (nitrogen or argon) atmosphere at a pressure of 30–60 atm. Boric oxide is used as flux.

Workers at the Nippon Telegraph and Telephone Public Corporation (Japan) have grown single crystals of indium phosphide in MSR6R high-pressure assemblies (Metals Research, England) using resistance heating. The temperature of the melt in the quartz crucible was kept constant to within ±0.1 K using a thermocouple placed at the bottom of the crucible. The starting material, synthesised by HZF, with $n = (8–40) \times 10^{15}$ $cm^{-3}$ (300 K), was placed in crucibles with diameter 50 mm or 100 mm (95 g and 300 g respectively). The thickness of the layer of flux varied from 6 mm to 24 mm.[20–22] Single crystals of indium phosphide were grown in the crystallographic direction <111>; the seed was raised at a rate of 10–12 mm $h^{-1}$. The crucible and the seed were rotated in the same direction at rates of 5 r.p.m. and 3 r.p.m. respectively. A nitrogen pressure of 35 atm was maintained in the chamber. This gave non-doped single crystals of indium phosphide with diameter 25 mm, with $n = 4.8 \times 10^{15}$ $cm^{-3}$ and $u = 2.68 \times 10^4$ $cm^2$ $V^{-1}$ $s^{-1}$ (77 K).[22]

Specialists at Bell (USA) used an autoclave assembly with induction heating (450 kHz) to grow single crystals of indium phosphide. The original polycrystalline material with $n = (2–5) \times 10^{15}$ $cm^{-3}$ (77 K) was synthesised by HDC. The single crystals were grown in the crystallographic direction <111> under the following conditions: nitrogen pressure in the compartment 38 atm; seed raised at a rate of 13–17 mm $h^{-1}$; rate of rotation 20–30 r.p.m.; thickness of layer of flux 5 mm (15 g boric oxide). The crucibles, with diameter

38 mm, were made of quartz or PBN. The non-doped single crystals of indium phosphide with diameter 30 mm and 80 mm had $N_d = 7 \times 10^3 - 5 \times 10^5$ cm$^{-2}$.[1,2,23]

Single crystals of indium phosphide with large diameter (greater than 40 mm) have been grown in MSR6R and Melbourn (England) assemblies. In the first assembly, crystals were grown in the crystallographic directions <111> and <100> in quartz or PBN crucibles with height and diameter 100 mm, containing the original polycrystalline indium phosphide (1 kg). Crystallisation at a rate of 9 mm h$^{-1}$ gave non-doped single crystals of indium phosphide with diameter 45–60 mm, mass 800 g, and $N_d = (1-10) \times 10^4$ cm$^{-2}$.[10]

Single crystals of indium phosphide with diameter 80 mm and mass 3 kg were grown in the Melbourn apparatus from crucibles with height and diameter 150 mm containing the original polycrystalline indium phosphide (3.5 kg). The density of dislocations in these crystals was $(3-8) \times 10^4$ cm$^{-2}$.[10]

The main technical difficulty in the growth of single crystals of indium phosphide by LHM is twinning of the crystals in the initial stage of growth. When the process is carried out in the crystallographic direction <111>, to prevent twinning, the crystal is grown from a seed to a constant diameter at an angle ≤19° 68′ relative to the growth axis.[1,2,20–28] These growth conditions prevent twinning along the (111) planes (Fig. 4), which lie at an angle of 70° 32′ to the direction of growth.

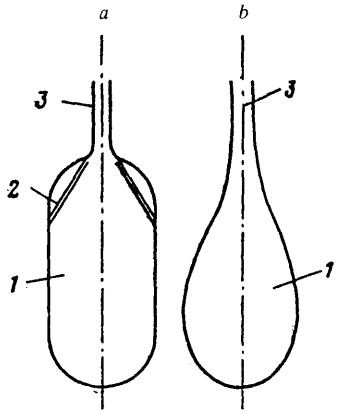



**Figure 4.** Profile of single crystals of indium phosphide grown from the seed to the nominal diameter in the <111> direction at an angle greater than (a) and less than (b) 19° 68′: *1*) single crystal, *2*) twinning planes, *3*) seed.[2]

When single crystals of indium phosphide are grown in the crystallographic direction <100>, the probability of twinning is reduced considerably if the crystal is grown from the seed to a constant diameter without vertical movement of the seed (angle of growth relative to the growth axis ~90°).[10]

During growth, twins may be produced in the crystal as a result of the introduction into the crystallisation front of foreign inclusions (oxides, gas bubbles, etc.) present on the surface of the molten indium phosphide. Special preparation of the flux to obtain a pure melt (without bubbles) has been carried out in a platinum crucible at 1000 °C in a vacuum for 24 h.[1,29] Before use, the boric oxide was kept in a quartz ampoule in a vacuum at $5 \times 10^{-6}$ mmHg. The residual bubbles were removed from the flux by rotating the seed at an increased rate (greater than 20 r.p.m.).

The thermal decomposition of the indium phosphide single crystal after its removal from under the layer of flux may lead to the flow of the free indium liberated along the crystal to the crystallisation front.[21] Thus to prevent decomposition of the surface of the single crystal of indium phosphide it is necessary, after removing it from under the layer of flux, to cover it with a thin layer of flux. To achieve this, the temperature of the flux must be kept at ~550 °C.

The probability of twinning in single crystals of indium phosphide is reduced by decreasing the thermoelastic stresses produced during growth, and also by doping the indium phosphide with strengthening impurities such as zinc and sulphur (not more than $10^{18}$ atom cm$^{-3}$ [29] or antimony $(1.7-7.2) \times 10^{-3}$ mass %.[30]

## 2. Preparation of Highly Pure Non-Doped Single Crystals of Indium Phosphide

During the growth of single crystals of indium phosphide by LHM, the product is contaminated by impurities entrained by the faces of the granules of the original polycrystalline material and impurities present in the flux (boric oxide).[29] Another source of contamination is the volatilisation of impurities from the graphite screens.[15] Thus when screens previously heated in a vacuum at 1300 °C were used, the concentration of principal charge carriers in indium phosphide was lowered by a factor of approximately two. Silicon is the chief background impurity, and it produces marked changes in the characteristics of instruments based on indium phosphide:[15,21,22,29] the concentration of silicon is $(6-16) \times 10^{15}$ atom cm$^{-3}$.[22,31]

During the growth of single crystals in a quartz crucible, silicon is transferred to the melt as a result of a reaction between indium phosphide and silicon(IV) oxide.[15] To decrease the concentration of silicon in the melt and the crystal, PBN crucibles are used. Another source of silicon is low-melting borosilicate glass, a thin layer of which is formed on the walls of the quartz crucible.[32] Since the chemical bond between silicon and oxygen is weaker in this layer, the transfer of silicon to the indium phosphide melt is facilitated. An increase in the concentration of silicon in the flux (boric oxide) has been detected after indium phosphide crystals have been grown in a quartz crucible. In the flux situated at the centre of the crucible, the silicon concentration was 62 times that in the original boric oxide, and at the wall of the quartz crucible the corresponding factor was 2200. When PBN crucibles were used, the concentration of silicon in the flux after the growth of indium phosphide crystals remained unchanged. This confirms that PBN crucibles must be used to grow highly pure indium phosphide crystals by LHM.

A change in the nature of the distribution of silicon in a crystal grown in a PBN crucible has been detected:[32] the effective distribution coefficient increased to $k > 1$. This change is apparently due to the extraction of silicon from the indium phosphide melt by the boron(III) oxide flux.

It should however be noted that the use of PBN crucibles leads to appreciable contamination of indium phosphide by boron, and in some cases to the appearance of traces of a second phase during growth, as a result of the reaction of boric oxide with PBN.[9]

To increase the purity of indium phosphide, melts with non-stoichiometric composition have been crystallised;[33] the original polycrystalline material, synthesised by HZF in a high-pressure assembly, was crystallised (at a rate of 6 mm $h^{-1}$) by LHM with the addition of 10 mass % and 20 mass % indium. The addition of 20 mass % indium gives best results. In the first case (10 mass % indium), original material with $n = 4 \times 10^{15}$ $cm^{-3}$ and $u = 1.815 \times 10^{4}$ $cm^2$ $V^{-1}$ $s^{-1}$ (77 K) gave an indium phosphide crystal with $n = 3.24 \times 10^{15}$ $cm^{-3}$ and $u = 3.015 \times 10^{4}$ $cm^2$ $V^{-1}$ $s^{-1}$ (77 K). In the second case (20 mass % indium), a material with $n = 9.02 \times 10^{15}$ $cm^{-3}$ and $u = 7.5 \times 10^{3}$ $cm^2$ $V^{-1}$ $s^{-1}$ gave a crystal with $n = 9.36 \times 10^{15}$ $cm^{-3}$ and $u = 1.517 \times 10^{4}$ $cm^2$ $V^{-1}$ $s^{-1}$ (77 K). The concentration of silicon in the best indium phosphide specimens obtained by LHM was (1.0–1.5) $\times 10^{-6}$ at.% or (2–3) $\times 10^{14}$ atom $cm^{-3}$.

### 3. Production of Doped Single Crystals of Indium Phosphide

To obtain single crystals with electron and hole conductivity and a high concentration of principal charge carriers, used to produce optoelectronic instruments, indium phosphide is doped with the donor impurities tin and sulphur and the acceptor impurity zinc (see Table).

Parameters of single crystals of indium phosphide with diameter 40–55 mm, produced by Sumimoto (Japan) in 1982.[34]

| Dopant | Electrophysical parameters at 300 K | | | Dislocation density, $cm^{-2}$ (not more than) |
|---|---|---|---|---|
| | concentration of principal charge carriers, $cm^{-3}$ | mobility of principal charge carriers, $cm^2V^{-1}s^{-1}$ | specific resistance, Ω.cm | |
| Tin | $5\times10^{17}$–$6\times10^{18}$ | 1200–2500 | $5\times10^{-4}$–$6\times10^{-3}$ | $5\times10^{4}$ |
| Sulphur | not less than $2 \times 10^{18}$ | 800–1800 | not more than $1.8 \times 10^{-3}$ | $5\times10^{3}$ |
| Zinc | not less than $2 \times 10^{18}$ | 35–60 | not more than $5 \times 10^{-2}$ | $5\times10^{3}$ |
| Zinc | $1\times10^{18}$–$5\times10^{18}$ | 80–150 | 1.5–80 | $5\times10^{4}$ |

In the USSR, single crystals of indium phosphide doped with tellurium are also used (diameter 20–40 mm; length not less than 25 mm), with $n = (5–500) \times 10^{16}$ $cm^{-3}$, $u = (1$ to $2.5) \times 10^{3}$ $cm^2$ $V^{-1}$ $s^{-1}$ (300 K), and $N_d < 5 \times 10^{4}$ $cm^{-2}$.

Doping indium phosphide with iron and chromium impurities gives single crystals with a high specific resistance. The specific resistance (ρ) of single crystals of indium phosphide doped with chromium does not exceed $5 \times 10^{3}$ Ω.cm,[35] whereas doping with iron gives a material with $\rho > 10^{7}$ Ω.cm.[2,15,19,35–38] Thus iron is usually employed to obtain semi-insulating indium phosphide.

Single crystals of semi-insulating indium phosphide have been grown by LHM in the crystallographic directions <111> and <100>. The starting material was indium phopshide with maximum purity ($n = 5 \times 10^{15}$ $cm^{-3}$ and $u = (2.5–3.5) \times 10^{4}$ $cm^2$ $V^{-1}$ $s^{-1}$),[15,34] giving crystals with $\rho > 10^{7}$ Ω.cm with a low concentration of iron in the melt (0.002–0.04 mass %).

Fig.5 gives the dependence of the specific resistance of indium phosphide on the proportion of crystallised melt for different concentrations of iron in it. To obtain crystals with $\rho > 10^{7}$ Ω.cm along the entire length it is evidently necessary to add 0.02–0.04 mass % iron to the melt. With increase in the concentration of iron in the melt to 0.1 mass %, the production of single crystals is made difficult by twinning as a result of non-metal inclusions on the surface of the melt.[15] To ensure thermal stability of the material during annealing after iron implantation, it is necessary to lower the iron concentration to 0.022 mass %. If the iron concentration in the crystal exceeds $8.8 \times 10^{15}$ atom $cm^{-3}$, then the specific resistance after annealing the indium phosphide specimens at 750 °C is lowered.[36]

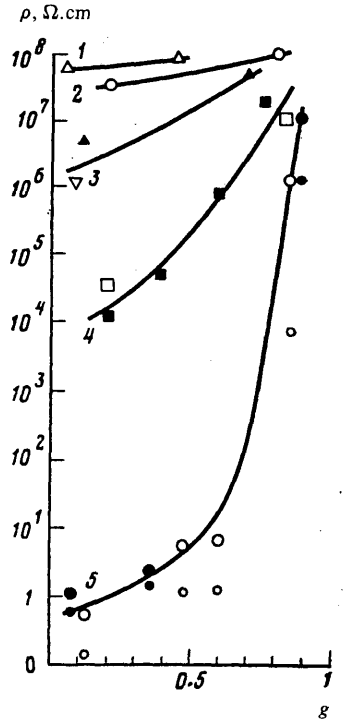



**Figure 5.** Distribution of the specific resistance along the length of a single crystal (*g*) of semi-insulating indium phosphide doped with iron (mass % in the melt): *1*) 0.15; *2*) 0.04; *3*) 0.02; *4*) 0.01; *5*) 0.005.[15]

Single crystals of semi-insulating indium phosphide with diameter 45–55 mm have been grown in the crystallographic direction <100> in autoclave assemblies under a nitrogen pressure of 50 atm (seed raised at a rate of 7–10 mm $h^{-1}$, rate of rotation of the seed and the crucible 7–15 r.p.m.) from under a layer of flux with thickness 18–20 mm. The temperature gradient in the region of the flux–melt boundary was about 100 K $cm^{-1}$. The dislocation density was (2–4) $\times 10^{4}$ $cm^{-2}$ in the initial section of the ingots, and (6–15) $\times 10^{4}$ $cm^{-2}$ in the final section.[36]

Polycrystalline indium phosphide with $n = (2–4) \times 10^{15}$ $cm^{-3}$ and $u = (2.5–3.0) \times 10^{4}$ $cm^2$ $V^{-1}$ $s^{-1}$ (77 K) has been used[26] to obtain cobalt-doped ($2 \times 10^{-3}$ mass %) semi-insulating indium phosphide with $\rho > 10^{7}$ Ω.cm. The effective distribution coefficient of cobalt in the indium phosphide was $4 \times 10^{-5}$, and the concentration of cobalt in the initial section of the crystal was $4 \times 10^{15}$ atom $cm^{-3}$. At this concentration of cobalt in the crystals, however, there was considerable separation of secondary phases—cobalt(III) phosphide and

phases of indefinite structure containing 70 mass % phosphorus and 30 mass % cobalt.[26,39] The separation of secondary phases began approximately half way along the length of the ingot.

### 4. Preparation of Low-Dislocation and Dislocation-Free Single Crystals of Indium Phosphide

To obtain low-dislocation and dislocation-free semiconductor single crystals, the thermoelastic stresses $\tau_{te}$ produced in the crystal during growth and cooling should not exceed the critical stresses of dislocation formation $\tau_{cr}$. The values of $\tau_{te}$ can be lowered, and the minimum density of dislocations in single crystals of indium phosphide obtained, by growing under temperature conditions ensuring the minimum axial and radial temperature gradients.

Dislocation-free non-doped single crystals of indium phosphide with diameter not greater than 15 mm have been obtained by growing a thin "neck" on the seed.[20-22] This method made it possible to obtain dislocation-free single crystals on seeds with a dislocation density of $10^5$ cm$^{-2}$. After the annihilation of the dislocations in the "neck", new dislocations were produced in the crystal when the diameter exceeded the critical value, which depends on the axial and radial gradients. Small temperature gradients $\partial T/\partial x$ were achieved by increasing the thickness of the layer of boric oxide ($\delta$). Thus for $\delta$ = 6 mm, $\partial T/\partial x$ = 175 K cm$^{-1}$, which ensured the production of non-doped dislocation-free single crystals of indium phosphide with diameter 8 mm. At $\delta$ = 13 mm and $\partial T/\partial x$ = 55 K cm$^{-1}$, the diameter of the dislocation-free crystals increased to 15 mm.[21]

A theoretical calculation[21] has shown that to obtain non-doped dislocation-free single crystals of indium phosphide with diameter 25 mm it is necessary to decrease the temperature gradient to 20 K cm$^{-1}$, or to 5 K cm$^{-1}$ for a diameter of 50 mm. It is practically impossible, however, to achieve these gradients, either by increasing the thickness of the layer of flux or by other methods. Thus the maximum diameter of non-doped dislocation-free single crystals of indium phosphide is not greater than 15 mm. With increase in the diameter of the crystal, dislocations are generated at the periphery of the ingot and multiply into the depth of the crystal.

The dislocation density in indium phosphide crystals with a large diameter (>40 mm) during growth has been reduced using a system for automatically controlling the diameter by weighing the crucible.[15,24-27,36] The stresses in the crystal after growth were removed by annealing at a high inert-gas pressure (~38 atm).[2,23] This decreased the dislocation density by a factor of approximately ten.[2]

A more promising method for decreasing the dislocation density in indium phosphide is by increasing $\tau_{cr}$ by doping with strengthening impurities. Impurity atoms with dimensions smaller than those of the atoms of the components of the semiconducting compound being replaced lower considerably the dislocation density in single crystals of these compounds. The same applies to a lesser extent to large atoms (Fig.6).[40] Zinc, sulphur, and germanium are used as impurities of this kind.[24,41,42]

Calculation shows that the maximum thermoelastic stresses produced during the growth of single crystals of indium phosphide correspond to 800 °C. The difference in the values of $\tau_{cr}$ for non-doped single crystals and single crystals doped with zinc ($2 \times 10^{18}$ atom cm$^{-3}$) is extremely large (Fig.7). This calculation confirms the temperature range of dislocation formation obtained by analysing the characteristic features of the dislocation structure.[42]

Increase in the concentration of zinc to $10^{19}$ atom cm$^{-3}$ and of sulphur to $10^{19}$ atom cm$^{-3}$ has been used to obtain dislocation-free single crystals of indium phosphide with a diameter of not more than 30 mm.[41] Combined doping with zinc and sulphur to a total concentration of $2 \times 10^{19}$ atom cm$^{-3}$ made it possible to lower the dislocation density in single crystals of indium phosphide with diameter 30 mm to $10^2$–$10^3$ cm$^{-2}$.[43]

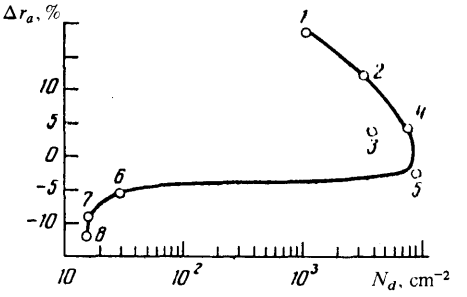



**Figure 6.** Influence of the difference between the tetrahedral radii of the impurity and the atom of the compound being replaced ($\Delta r_a$) on the dislocation density ($N_d$) in single crystals of indium phosphide and gallium arsenide doped with various elements: *1*) InP(Te); *2*) GaAs(Te); *3*) InP(Se); *4*) GaAs(Zn); *5*) InP(Sn); *6*) InP(S); *7*) InP(Zn); *8*) GaAs(S).[40]

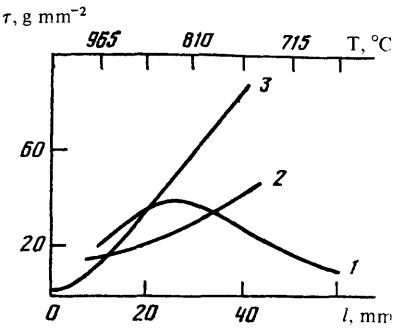



**Figure 7.** Comparison of the thermoelectric stresses ($\tau_{te}$) along the axis of indium phosphide crystals and the critical stresses of dislocation formation ($\tau_{cr}$) at corresponding temperatures at a distance $l$ from the crystallisation front: *1*) $\tau_{te}$; *2*) $\tau_{cr}$ for non-doped indium phosphide; *3*) $\tau_{cr}$ for indium phosphide doped with zinc ($p = 2 \times 10^{18}$ cm$^{-3}$).[42]

Single crystals of indium phosphide with diameter 26 mm, doped with germanium ($1.5 \times 10^{17}$–$1.6 \times 10^{19}$ atom cm$^{-3}$), have been grown in the crystallographic direction <111>.[24] Dislocation-free crystals were obtained with $n = 1.1 \times 10^{19}$ cm$^{-3}$ and $n = 1.6 \times 10^{19}$ cm$^{-3}$; in other cases the dislocation density was $(2.2–5) \times 10^4$ cm$^{-2}$. Decrease in the dislocation

density began at a germanium concentration greater than $7 \times 10^{18}$ atom $cm^{-3}$. A disadvantage of doping with germanium is that large defects (>50 nm) of unusual shape (oval), lying on dislocation lines, appear in the indium phosphide structure.[25,27,37,42,44] Thus in practice, doping with zinc and sulphur is used to decrease the dislocation density in indium phosphide. In Japan, low-dislocation single crystals of indium phosphide with $N_d < 10^2$ $cm^{-2}$ and diameter 20–30 mm have been obtained on the industrial scale.

Attempts to dope indium phosphide with isovalent impurities, which have been used successfully to dope gallium arsenide (antimony, arsenic, etc.), have not yet given satisfactory results.[45]

### 5. Some Characteristic Features of the Dislocation Structure of Single Crystals of Indium Phosphide

Selective chemical etching of indium phosphide specimens has revealed several types of etch pit, corresponding to linear dislocations, dislocation loops, and dislocation clusters. In addition, in some specimens, *s*-shaped etch pits of non-dislocation character (fine-point background) have been detected. This background has been observed in single crystals of indium phosphide doped with tin ($2 \times 10^{18}$ atom $cm^{-3}$; density of *s*-shaped etch pits $6 \times 10^4$ $cm^{-2}$) and sulphur ($10^{19}$ atom $cm^{-3}$; density of *s*-shaped etch pits $2 \times 10^3$ $cm^{-2}$).[41]

Structural defects of the dislocation cluster type have been detected by selective chemical etching and X-ray topography both in non-doped indium phosphide single crystals and in specimens doped with germanium, tin, iron, and selenium.[21,25,27,37,41,44] The size of the clusters varied from 5 nm to 200 nm. They consist of a central region, surrounded by prismatic dislocation loops, ordered along twelve <110> axes. The central region consists of a compact accumulation of dislocations, and contains complexes of two types: triangular, with dimensions 0.5–8 nm, and spherical, with dimensions 5–8 nm.[25,40] The chemical nature of the clusters is not clear, but studies have shown that there is an excess of indium at the points where they are situated. A model has been proposed[37] for the production of the clusters, based on the interaction of antistructural defects with moving dislocations.

Dislocation clusters with a density of $10^2$–$10^3$ $cm^{-3}$ have been detected[27] in non-doped single crystals of indium phosphide and in specimens doped with germanium. No relationship was detected between the germanium concentration and the appearance of the clusters. The distribution of the clusters along the length of the ingot was regular, although some specimens showed a decrease in their density towards the end of the ingot. The density of the clusters increased with increase in the quantity of macroscopic defects (such as twins). After annealing the specimens at 800 °C for 1, 4, and 8 h, the density of the clusters increased from $1.8 \times 10^2$ $cm^{-2}$ to $4.3 \times 10^2$ $cm^{-2}$. If the specimen did not contain clusters, they were not formed during annealing. An important characteristic of the annealing was the increase in the size of the clusters as a result of the enlargement of the dislocation loops, and not an increase in the number of dislocations.

In the opinion of the authors cited,[25,27] the main reason for the appearance of clusters is the presence of water in the flux. The reaction of water with indium phosphide gives phosphorus vapour, whose inclusion leads to the production of stresses and to the formation of clusters. Dehydrating the flux by heating made it possible to obtain crystals without dislocation clusters.

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# The Oxidative Cleavage of the Silicon-Silicon Bond

G.A.Razuvaev, T.N.Brevnova, and V.V.Semenov

Data on the oxidative cleavage of single and double silicon-silicon bonds in inorganic and organic polysilanes with linear and cyclic structures have been summarised. Particular attention has been paid to studies in which the mechanisms of the oxidation are discussed. The nature of the silicon-silicon bond in organopolysilanes and disilenes has been briefly reviewed. The bibliography contains 248 references.

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## I. INTRODUCTION

Compounds with silicon–silicon bonds have not yet found such wide application as, for example, organopolysiloxanes, but the chemistry of compounds of this class[1-23] is now being intensively developed. Important recent achievements include the synthesis of stable disilenes, that is compounds with a silicon–silicon double bond.[24,25] The possible use of polysilanes to obtain silicon carbide materials,[26-30] as components of catalytic systems for the polymerisation of ethylene hydrocarbons,[31,32] and as stabilisers of polyvinyl chloride,[33] silylating and reducing reagents,[34] and also semiconductors,[35-36] is being studied.

The aim of the present review is to show how the reactivity of the Si–Si bond with respect to oxidation reactions of different types depends on the type of polysilane, the substituents on the silicon atom and in the organic group, the size of the ring, the length of the $-(-\mathrm{Si}-)_n-$ chain, and various other factors. Of greatest interest in this connection are studies in which the mechanisms of the oxidation reactions are discussed, and also studies from which it is possible to reach definite conclusions about the influence of the structure of the polysilane on its reactivity. Material on the application of reactions of this type in synthesis have not been considered, since this topic has been dealt with in detail in a number of reviews.[1,2,7-9,17,18] The photochemical and thermal reactions of polysilanes, taking place via radical, silylene, and sila-alkene intermediates, are discussed very briefly. The review does not deal with reactions taking place under the influence of catalysts.

Extensive material on the study of the properties of the Si–Si bond by spectroscopic methods has now accumulated. The use of spectroscopic data is extremely fruitful in the examination of the reactivity of polysilanes. For this reason, a separate section deals briefly with the properties of the silicon–silicon bond, based chiefly on ultraviolet spectroscopic data.

## II. THE NATURE OF THE SILICON–SILICON BOND

In 1962, the ultraviolet spectrum of hexaphenyldisilane was found to contain a band at 240 nm,[37] not observed for tetraphenylsilane. At first, the authors cited attributed the appearance of this band to strong interactions between the phenyl groups via the 3*d* atomic orbitals (AO) of the two silicon atoms of the disilane bridge. It was subsequently shown,[38-40] however, that the absorption in the region of 240 nm is characteristic of the $-(-\mathrm{SiR_2}-)_n-$ and $\mathrm{Ph}-(-\mathrm{SiR_2}-)_n-$ systems, that is that the chain of silicon atoms itself shows chromophoric properties and also undergoes conjugation with the π-electrons of the aromatic ring. Increase in the length of the polysilicon chain and the pres- of phenyl or vinyl substituents at its ends displace the absorption band maximum to longer wavelengths. The ultraviolet spectra of linear and cyclic organopolysilanes with different substituents on the silicon atoms,[41-57] and compounds containing chains of other group IVb elements (Ge, Sn, Pb),[58,59] have been studied. The photoelectron spectra (PES) and electronic absorption spectra of charge-transfer complexes (CTC) show that the electrons of the silicon–silicon bond have a relatively low first ionisation potential (8.69 eV for hexamethyldisilane), which decrease with increase in the polysilane chain length. These data indicate that the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of polysilanes approach one another with increase in the number of silicon atoms. A similar phenomenon is observed more clearly in conjugated polyenes. In alkanes also, there is a slight displacement of the absorption maximum towards longer wavelengths. It was therefore concluded[55,60] that as in saturated hydrocarbons, in polysilanes there is delocalisation of electrons through the $\sigma_{C-C}$ or $\sigma_{Si-Si}$ bonds, the delocalisation being very slight in alkanes, but considerable in polysilanes. Thus the $-(-\mathrm{MR_2}-)_n-$ (M = Si, Ge, Sn) systems as it were occupy an intermediate position between saturated hydrocarbons and polyenes, that is they show signs of "double-bond character".

The unoccupied 3*d* AO of silicon have been used to explain the delocalisation of electrons along the $-(-\mathrm{SiR_2}-)_n-$ chains. For example, the absorption in the region of 240 nm has been attributed[39,41] to transitions of the π or $\sigma_{Si-Si}$ electrons of the $\mathrm{Ph}-(-\mathrm{SiR_2}-)_n-$ fragment into non-bonding molecular orbitals formed by the combination of unoccupied 3*d* AO of the silicon atoms; the possible partial transfer of the electron density of the $\sigma_{Si-Si}$ bond into the 3*d* AO and delocalisation through the system of *d* orbitals of silicon in the ground state: Si–Si ↔ Si⋯⋯Si have been assumed.[4,5] It has been suggested[61-64] that the π electrons of multiple bonds or

the lone pairs of electrons of the oxygen atoms in alkoxypolysilanes may be partly transferred not only to the first silicon atom ($p_\pi$, $d_\pi$ conjugation) but also to subsequent atoms ($p_\pi$, $d_\pi$, $d_\pi$ conjugation). It has been shown,[65] however, that to explain the photoelectron spectra of permethylsilanes it is not necessary to introduce the unoccupied 3*d* AO of silicon. Electron delocalisation can take place through the system of $\sigma_{Si-Si}$ bonds ($\sigma$, $\sigma$ conjugation).[20-22] For example, in octamethyltrisilane the original level of the $\sigma_{Si-Si}$ electrons ($\alpha_{Si-Si}$ = 8.69 eV) is split into two $\sigma$-orbital levels $\alpha_{Si-Si} + \beta$ and $\alpha_{Si-Si} - \beta$. A quantitative expression of the interaction of two $\sigma_{Si-Si}$ bonds is provided by the magnitude of the resonance integral $\beta_{Si-Si}$, which has been estimated as −0.5 eV.[65]

It has been shown[14,15,56,66-73] that a system of $\sigma_{Si-Si}$ bonds can interact with different $\pi$- and *n*-electron systems (phenyl, naphthyl, vinyl, −O−, −S−). Analysis of data obtained from the photoelectron spectra and electronic absorption spectra of CTC shows that significant interaction of a $\sigma_{Si-Si}$ bond with $\pi$- and *n*-electron systems takes place at differences in the levels of the HOMO ($\Delta E$) of the interacting fragments up to 0.5–0.6 eV. At these $\Delta E$ values, the $\sigma_{Si-Si}$–$\pi$ or $\sigma_{Si-Si}$–*n* interaction is 0.25–0.72 eV. At $\Delta E$ = 1 eV or more, the $\sigma_{Si-Si}$–$\pi$ interaction is slight, and amounts to less than 0.1 eV. In the ultraviolet spectrum of a substituted disilane, the long-wave absorption maximum may undergo an appreciable bathochromic shift, as for example in vinylpentamethyldisilane and 1,2-divinyltetramethyldisilane.[73] The displacement of the absorption maximum to longer wavelengths without a significant change in the first ionisation potential of substituted polysilane is attributed to the interaction of the $\sigma^*_{Si-Si}$ and $\pi^*$ molecular orbitals.[73]

The high polarisability of the silicon–silicon bond is revealed by the ability of organopolysilanes to form charge-transfer complexes with various electron acceptors, for example tetracyancethylene,[74,75] and by their higher reactivity, compared with aliphatic hydrocarbons. Some similarity in chemical behaviour between Si–Si and C=C bonds can be demonstrated for reactions with such electrophilic reagents as peroxybenzoic acid and bromine. The reaction takes place with cleavage of the Si–Si or C=C bonds via the formation of donor–acceptor complexes, in which electron density is transferred from the $\sigma_{Si-Si}$ or $\pi_{C-C}$ bonds to the molecular orbitals of the electrophile.

$$R_3SiSiR_3 + PhCO_3H \rightarrow R_3SiOSiR_3 + PhCOOH$$

$$R_3SiSiR_3 + Br_2 \rightarrow 2R_3SiBr$$

$$RCH{=}CH_2 + PhCO_3H \rightarrow RCH(O){-}CH_2$$

$$RCH{=}CH_2 + Br_2 \rightarrow RCH(Br){-}CH_2(Br)$$

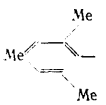
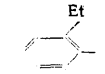
At the same time, organopolysilanes also take part in transformations characteristic of saturated hydrocarbons, for example isomerisation.[11]

$$Me_3SiSiMe_2SiMe_2SiMe_3 \xrightarrow{AlCl_3} (Me_3Si)_3SiMe$$

$$MeCH_2CH_2Me \xrightarrow{AlCl_3} Me_3CH$$

In 1981, West and co-workers reported the synthesis of tetramesityldisilene, the first stable compound with a silicon–silicon double bond.[24,25] This was followed by the preparation of several more representatives of this class of compound, including some with alkyl substituents. The chief factor leading to stabilisation of the Si=Si bond is the presence of bulky substituents on silicon. Some physicochemical characteristics of a number of disilenes are given in the Table.[76-89] The Si=Si bond length is approximately 0.18–0.20 Å shorter than the typical silicon–silicon single bond length.[78,84] The decrease in length due to $\pi$-bonding is 8–9% for disilenes, and about 12% for alkenes.[78] The four Si–C bonds in tetramesityldisilene are approximately coplanar.[76,79] From data on the measurement of the anisotropy of the $^{29}$Si chemical shift it was concluded that the electronic structures of the Si=Si and C=C bonds are completely analogous.[79] The contribution of the $\pi$–component is considerable.

Physicochemical characteristics of disilenes $R_2Si{=}SiR_2$.

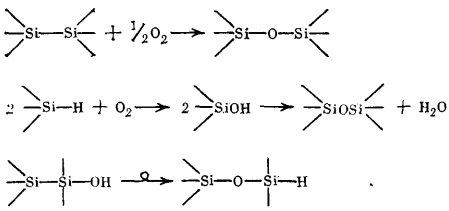
| R | $r_{Si=Si}$, Å | $\lambda_{max}$, nm | M.p., °C | Refs. |
|---|---|---|---|---|
|  | 2.16 | 420 | 178 | [24,25, 76–79] |
|  | — | 422 | 216–217 | [80,82] |
|  | 2.14 | 426 | 201–204 | [84] |
| $Me_3CCH_2$— | — | 400 | — | [85] |
| $Me_3C$— | — | 433 | — | [83,87] |
| $Me_2CH$— | — | 400 | — | [86] |
| $Et_2CH$ | — | 390 | — | [81] |

All prepared disilenes, in solution or the solid state, are bright yellow. The ultraviolet absorption maximum lies at 400–430 nm, and for aryl derivatives it is displaced to longer wavelengths as a result of the perturbation produced by the $\pi$-system of the aryl groups (an exception is tetra-t-butyldisilene, for which an unusually high value of $\lambda_{max}$ = 433 nm is observed[83]). The absorption band in the range 400–430 nm is evidently due to a $\pi$–$\pi^*$ transition, whose energy is much lower in disilenes than in alkenes. The first ionisation potential ($I_1^D$) of tetrakis(2,6-dimethylphenyl)-disilene (8.40 eV)[83] is close to the known values for phenyl-substituted disilanes: $Me_5Si_2Ph$ (8.39 eV), $PhMe_2SiSiMe_2Ph$ (8.23 eV).[90]

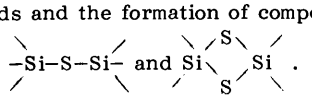
## III. THE OXIDATION OF INORGANIC COMPOUNDS CONTAINING A SILICON–SILICON BOND

Among inorganic silicon derivatives, the highest reactivity towards oxidising agents is shown by the hydrides, with linear, branched $Si_nH_{2n+2}$ ($n$ = 1–6),[3-5,7] and cyclic $(SiH_2)_n$ ($n$ = 5,6) structures.[18,91-93] They are rapidly decomposed by alkalis, and the reaction with oxygen and chlorine takes place with the production of flames or an explosion. The spontaneous flammability of silanes increases in the order $SiH_4 < Si_2H_6 < Si_3H_8$.[3-5] Disilane derivatives such as disilanyl ether $(Si_2H_5)_2O$, bis(disilanyl) sulphide $(Si_2H_5)_2S$, tris(disilanyl)amine $(Si_2H_5)_3N$, and

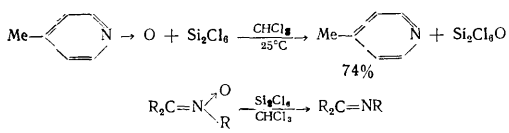
iododisilane $Si_2H_5I$ are also very sensitive to oxygen.[3] The polymeric silicon hydrides $(SiH_m)_n$ ($m = 1-2$), obtained by different methods,[4,5] are also oxidised in air. The rate of oxidation may vary over a wide range, depending on the method of preparation and the Si/H ratio. In the reaction of amorphous polysilane $(SiH)_n$ with oxygen, three types of transformation are assumed:[4,5,94]



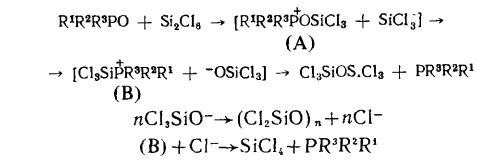
Oxidative cleavage of the Si–Si bond as a result of rearrangement is also possible for polysilanes with alkoxy or thiol groups.[6,16,17,95] In some cases of this kind the reactions are explosive.[16,17] A necessary condition for these rearrangements to take place is the fullest possible replacement of all the remaining valences in the $-(-Si-)_n-$ chain by OH, OR, or SR groups.

Halogenopolysilanes[6,18,19,23,96-99] are much more stable to oxygen than the corresponding silicon hydrides. The perfluorinated compounds are most easily oxidised. Decafluorotetrasilane and the subsequent members of the series, and also the higher fluorides of silicon $(SiF_2)_n$ and $(SiF)_n$ inflame spontaneously in air.[6,100] Perchloropolysilanes react with oxygen much more slowly. For example, the subchloride $(SiCl_2)_n$ inflames in a dry air atmosphere only when heated to 150 °C.[6] The reaction of the subhalides $(SiCl_2)_n$ and $(SiBr_2)_n$ with sulphur[6] takes place at an increased temperature (~170 °C) with cleavage of the Si–Si bonds and the formation of compounds containing the fragments  .

Hexachlorodisilane has been proposed as a reducing agent for the synthesis of organic derivatives of nitrogen, sulphur, and phosphorus.[101-104] The possibilities provided by the method are demonstrated by some examples given below.



The products are obtained in high yields. The reduction takes place rapidly and under mild conditions. This last feature is particularly important for preparing optically active phosphines and their oxides, since racemisation takes place at increased temperatures. The reduction of acyclic phosphine oxides takes place with inversion of the configuration and with a high stereospecificity. The proposed[102] mechanism of reduction includes several successive stages. The reaction begins with nucleophilic attack by the oxygen atom of the oxide on the silicon atom. The trichlorosilyl anion formed reacts with the intermediate (A) to give the trichlorosilylphosphonium cation (B) and a trichlorosiloxy-anion (inversion of the configuration at the phosphorus atom takes place at this stage). The $Cl_3SiO^-$ anion is 70% decomposed to perchloropolysiloxane $(Cl_2SiO)_n$ and $Cl^-$. The remaining 30% $Cl_3SiO^-$, and also $Cl^-$, react with the trichlorosilylphosphonium cation to give hexachlorodisiloxane, silicon tetrachloride, and the optically pure phosphine.



Phosphetane oxides and phosphine sulphides are reduced by hexachlorodisilane with complete preservation of the configuration at the phosphorus atom.[102] Reducing properties are also shown by perchloropolysilanes $Si_nCl_{2n+2}$ ($n > 2$) and by the vat residues from the direct synthesis of methylchlorosilanes.[105] The reactions of oxidative cleavage of the Si–Si bond in chloropolysilanes present in residues from direct synthesis have been reviewed.[106]

## IV. THE OXIDATIVE CLEAVAGE OF THE SILICON–SILICON BOND IN ORGANOPOLYSILANES

### 1. Oxidation of Organopolysilanes with a Linear Structure

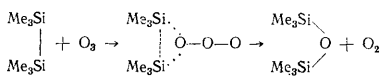
#### a) Reactions with oxygen and ozone

Peralkylated organopolysilanes with linear and branched structures are stable to atmospheric oxygen even at increased temperatures. Polysilanes containing the substituents OR, $CH{=}CH_2$, H, Cl, Br, and I in addition to alkyl and aryl groups on the silicon atoms also are not oxidised in air at room temperature. Fluoro-derivatives with the general formula $Si_2F_nMe_{6-n}$, containing two or more fluorine atoms, react with oxygen at 20 °C.[107] The reaction of 1,2-difluorotetramethyldisilane gives a mixture of products:

$$FMe_2SiSiMe_2F \xrightarrow{O_2} (FMe_2Si)_2O + (CH_2O)_n + H_2O + \text{polysiloxanes}$$

The isomeric 1,1-difluorotetramethyldisilane is oxidised much more slowly, and the main product is the corresponding disiloxane. 1,1,2-Trifluorotrimethyldisilane and 1,1,2,2-tetrafluorodimethyldisilane react with oxygen by a free-radical mechanism, analogous to that proposed for the oxidation of distannanes.[108]

Hexamethyldisilane reacts exothermally with ozone to give hexamethyldisiloxane in 95% yield. Bis(trimethylsilyl) peroxide was not found in the reaction products. The cleavage of the silicon–silicon bond by ozone takes place more readily than that of the Si–$C_{alkyl}$ bond. The marked difference in the oxidation rates ensures a high yield of hexamethyldisiloxane. It is assumed that the reaction takes place via a three-membered intermediate complex, and that ozone acts as an electrophilic reagent.[109]



The products and kinetics of the reactions of ozone with a number of organic derivatives of group IVb elements $R_4E$, $R_3EX$, $R_3EER_3$ (X = H, Cl, Br, OR; E = Si, Ge, Sn, Pb) in different solvents have been studied.[110-115] The reactions take place by a bimolecular heterolytic mechanism. The reactivity of the hetero-organic compound and ozone is increased by non-specific solvation. The sensitivity of the reaction to non-specific solvation is greater, the greater the reactivity of the hetero-organic compound (HOC) towards ozone. This result agrees with the suggestion that the polarity of the activated "HOC–ozone" complex is greater than that of the original reagents, and confirms that the

ozonolysis of the HOC takes place by a heterolytic mechanism. It has been shown that ozone takes part in the formation of the activated complex in an amphi-ionic form, in which the nucleophilic centre is localised chiefly on one oxygen atom. The values of the rate constants of reactions of $E_2Et_6$ (E = Si, Ge, Sn, Pb) with $O_3$ correlate satisfactorily with the values of the effective electronegativity of the heteroatom in these compounds, which increase in the order Pb < Sn < Ge < Si. The reactivity of the compounds decreases on going from Pb to Si.

b) Reactions with metal salts and oxides

Organopolysilanes reduce salts of mercury, nickel, platinum, and copper to the corresponding metals.[116–118]

$$Me_3SiSiPh_3 + Hg(OCOMe)_2 \xrightarrow{200^\circ C} Hg + Me_3SiOCOMe + Ph_3SiOCOMe$$
$$(MeO)_2MeSiSi(OMe)_2Me + CuCl_2 \rightarrow Cu + 2MeSi(OMe)_2Cl$$

Silver nitrate and vanadium(V) oxide oxidise disilanes to disiloxanes at increased temperatures.[116,117] Hexaphenyldisilane is very inert towards various oxidising agents. It begins to react with silver or sodium nitrate only when heated to 198 °C or 360 °C respectively.[119]

The oxidative cleavage of the Si–Si bond in polysilanes under the influence of tungsten and molybdenum chlorides has been studied.[120] The linear polysilanes $Si_nMe_{2n+2}$ ($n$ = 2, 3, 4, 6) and the branched polysilane $Si(SiMe_3)_4$ react exothermally with tungsten hexachloride or molybdenum pentachloride in benzene, chlorobenzene, or $CCl_4$ to give chlorosilanes and $WCl_4$ or $(MoCl_3)_x$. In decamethyltetrasilane, the terminal trimethylsilyl groups are removed first.

$$n\text{-}Si_4Me_{10} \xrightarrow{WCl_6} Me_3SiCl + ClMe_2SiSiMe_2SiMe_3$$

The product of the cleavage of octamethyltrisilane–pentamethylchlorodisilane–reacts with $WCl_6$ ten times more slowly than the original trisilane. A linear correlation was established between the first ionisation potentials of the polysilanes and the logarithms of the relative rate constants of the cleavage of the Si–Si bonds. Decrease in $I_1^D$ is accompanied by an increase in the rate of the reaction of the polysilanes with $WCl_6$, indicating that the rate-determining stage of the reaction is the transfer of the electrons of the $\sigma_{Si-Si}$ bond to $WCl_6$.

c) Reactions with halogens

Organopolysilanes are split by halogens to give halogenosilanes.[121–129]

$$R_3SiSiR_3 + X_2 \rightarrow 2R_3SiX$$
$$X = Cl, Br, I$$

When solutions of $Si_2R_6$ (R = Me, Et) and halogens ($Br_2$, $I_2$) are mixed, the ultraviolet spectrum shows a new strong charge-transfer band due to the donor–acceptor complex (DAC) $Si_2R_6.X_2$, not observed in the spectra of the starting materials and final reaction products.[126] In an excess of hexa-alkyldisilane, the rates of consumption of the DAC and the halogen are equal, indicating that the following equilibrium is rapidly established:

$$Si_2R_6 + X_2 \rightleftarrows Si_2R_6 \cdot X_2 .$$

The reaction is of first order with respect to each reagent, and takes place by a molecular mechanism, probably via the DAC detected, in which transfer of electron density takes place from the $\sigma_{Si-Si}$ bond to the molecular orbitals of the halogen.[126,129] The energy and entropy of activation for the reaction of 1,2-diphenyltetramethyldisilane with bromine in $CCl_4$ are 10.5 kcal mole$^{-1}$ and −25.4 e.u. respectively.[128]

The reactivity of the Si–Si bond in polysilanes towards halogens depends markedly on the nature of the substituents on silicon. Hexa-alkyldisilanes react very readily,[123,124] hexa-aryldisilanes react slowly,[123,130] and hexahalogenodisilanes react only at high temperatures.[6,123] The relative reactivity of the halogens decreases in the order $Cl_2 > Br_2 \gg I_2$.[8] In hydrogen-containing disilanes, the Si–H bond reacts first.[123]

$$R_3SiSiR_2H + X_2 \rightarrow R_3SiSiR_2X + HX$$
$$X = Br, I$$

Kinetic studies[122] have shown that the replacement of one methyl group in hexamethyldisilane by a chlorine atom decreases the rate of cleavage by iodine by a factor of approximately ten. The introduction of a second chlorine atom leads to a further decrease in the reaction rate. The silicon–silicon bond in $Cl_2MeSiSiMe_2Cl$ and $Cl_2MeSiSiMeCl_2$ is stable towards halogens.[6,9] On irradiation with light, the methyl groups are chlorinated. The rates of the reactions with halogens are increased by Friedel–Crafts catalysts.[123] In α,ω-dichloropermethylpolysilanes $Cl(Me_2Si)_nCl$ ($n$ = 4–6), the terminal Si–Si bond is less reactive towards chlorine than the inner Si–Si bonds, which are also split by the action of halogen. The relative reactivity of these compounds in chlorination[125] decreases with decrease in $n$: $6 \geq 5 \geq 4 > 3 \gg 2$. In $n$-decamethyltetrasilane, contrary to the result expected from the statistical factor, the inner Si–Si bond is split by bromine more rapidly.[123]

$$n\text{-}Si_4Me_{10} + Br_2 \rightarrow \begin{cases} 2Me_3SiSiMe_2Br\ 57\% \\ Me_3SiBr + BrMe_2SiSiMe_2SiMe_3\ 43\% \end{cases}$$

These data are consistent with electrophilic attack by the halogen on the polysilane molecule. There is a qualitative analogy with the electrophilic addition of halogens to a C=C bond.[131] In the reactions of polysilanes, the nucleophilic centre is the $\sigma_{Si-Si}$ bond. In spite of this, the opposite mechanism has been proposed[127] for the cleavage of aryl-substituted disilanes by bromine, where the silicon atoms of the Si–Si bond act as electrophile centres.

d) Reactions with acids and alkalis

In the reaction of hexamethyldisilane with concentrated sulphuric acid, one or two methyl groups are removed. Subsequent treatment of the reaction mixture with ammonium chloride gives pentamethylchlorodisilane and 1,2-dichlorotetramethyldisilane.[132] In the linear permethylpolysilanes $Me(Me_2Si)_nMe$ ($n$ = 2–4), partial rupture of Si–Si bonds takes place.[8] Gaseous HCl splits the Si–Si bond in permethylpolysilanes[8,9] only at high temperatures.

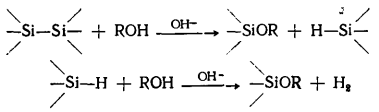
$$Me_3SiSiMe_3 + HCl \xrightarrow{450^\circ C} Me_3SiCl + Me_3SiH$$

Concentrated nitric acid reacts with hexamethyldisilane according to the equation:[8]

$$Me_3SiSiMe_3 + 2HNO_3 \rightarrow Me_3SiOSiMe_3 + 2NO_2 + H_2O$$

The reactivity of organopolysilanes towards aqueous and alcoholic solutions of alkalis[2,9,133] depends on the substituents on the silicon atoms. Electronegative substituents facilitate cleavage of the Si–Si bond. Peralkylated disilanes do not react with aqueous or alcoholic or alkali solutions, and the ethoxy-substituted $Si_2Me_n(OEt)_{6-n}$ react more rapidly, the smaller $n$; for example, hexa-acetoxydisilane[134] reacts

with aqueous NaOH solution with vigorous liberation of hydrogen. The reaction with alcoholic alkali solutions takes place according to the scheme:



The reaction is used for the quantitative determination of Si–Si bonds in various polysilanes. The reactions of alkalis with disilanes containing halogen atoms in the organic group are more complex.[135]

e) Reactions with oxides of nitrogen

Oxides of nitrogen split not only the Si–Si bonds but also Si–C bonds in alkylsilanes.[136]

$$Me_3SiSiMe_3 \xrightarrow{NO_2,\ 20^\circ C} Me_3SiOSiMe_3\ 95\%$$
$$Et_3Si{-}Et \xrightarrow{NO_2} Et_3SiOSiEt_3 + MeCOOH\ 90\%$$

The activity of the oxides in these reactions decreases in the order: $NO_2 > NO_3 > NO > N_2O$. Hexaphenyldisilane does not react with oxides of nitrogen in diethyl ether.[130]

f) Reactions with amine N-oxides

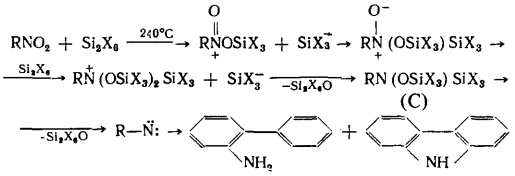
Trimethylamine oxide and pyridine N-oxide behave as nucleophilic reagents towards disilanes. A study of the oxidation of various *meta*- and *para*-substituted phenoxypentamethyldisilanes $Me_5Si_2OC_6H_4X$ by pyridine N-oxide[137] show that the reaction rate increases when electronegative substituents are introduced into the phenyl ring ($\rho = +1.18$). Vinylpentamethyldisilane is oxidised by trimethylamine oxide to vinylpentamethyldisiloxane; the vinyl group is unaffected.[137]

$$H_2C{=}CH{-}SiMe_2SiMe_3 \xrightarrow{Me_3NO} H_2C{=}CH{-}SiMe_2OSiMe_3$$

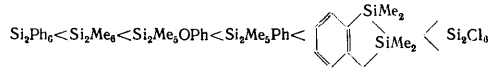
Organodisilanes can be used as reducing agents in the synthesis of various organic compounds.[138,139] Their reducing power is weaker than that of perchloropolysilanes. For example, hexamethyldisilane does not react with phosphine oxides[102] or amine N-oxides[137] at 70 °C. Aryl-substituted disilanes do not react with dimethyl sulphoxide on prolonged heating up to 100 °C.[140] On the other hand, hexachlorodisilane readily reduces these compounds even at room temperature.[102]

g) Reactions with aromatic nitro-compounds

The reducing properties of substituted disilanes with respect to aromatic nitro-compounds have been studied.[139] When a solution of the reagents in *o*-dichlorobenzene is heated to 240 °C, reaction takes place with the intermediate formation of a nitrene. The reaction mechanism proposed by the authors cited is fairly complex, and involves the nucleophilic attack by $RNO_2$ on silicon with subsequent heterolysis of the Si–Si bond. The nitrene is formed as a result of the removal of the disiloxane from the bis(silyl)hydroxylamine intermediate (C). [With 2-nitrobipherryl the products are as shown in the scheme. Ed.]



The reducing power of the disilanes is determined by their structure, and increases in the order:



Hexaphenyldisilane does not show reducing properties, probably because of the steric hindrance created by the phenyl groups. In contrast to this, the introduction of a substituent into the molecule of the compound being reduced in the *ortho*-position to the nitro-group has practically no influence on the rate of the reaction with hexamethyldisilane.

h) Reactions with hydrogen peroxide

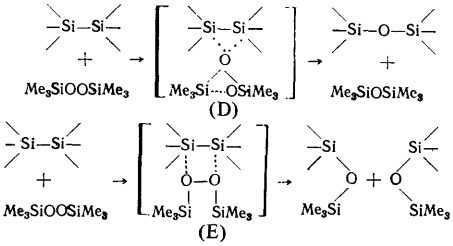
The silicon–silicon bond in permethylpolysilanes is not oxidised by hydrogen and sodium peroxides.[8,9] Hexaphenyldisilane is very inert towards various oxidising agents, and does not react with organic hydroperoxides and 30% $H_2O_2$ on boiling for 43 h in mixed THF–$CCl_4$ solvent.[119] Splitting takes place when an oxidising mixture consisting of $H_2O_2$ and NaOH in THF is used. The chief reaction products are triphenylsilanol and hexaphenyldisiloxane.

i) Reactions with bis(trimethylsilyl) peroxide (BTMSP)

Hexamethyldisilane reacts with BTMSP at 80 °C.[107]

$$Me_3SiSiMe_3 + Me_3SiOOSiMe_3 \rightarrow 2Me_3SiOSiMe_3$$

After 42 h in an excess of the peroxide, the extent of the transformation of hexamethyldisilane was 40%. Methylfluorodisilanes $Si_2F_nMe_{6-n}$ ($n = 1-4$) are oxidised by BTMSP even at temperatures from −10 °C ($n = 4$) to +20 °C ($n = 1, 2$).[107] The compounds with $n = 1, 2$ give the corresponding disiloxanes as chief products, whereas the oxidation of tri- and tetrafluorodisilanes ($n = 3, 4$) give in addition $Me_3SiF$, $Me_3SiOSiMe_2F$, and $Me_3SiOSiMeF_2$. The rate of the oxidation of 1,2-difluorotetramethyldisilane does not decrease when the inhibitor 2,4,6-tri(t-butyl)phenol is added. It is suggested that the reactions take place via the intermediate states (D) and (E). The oxygen atoms of BTMSP act as nucleophilic centres.



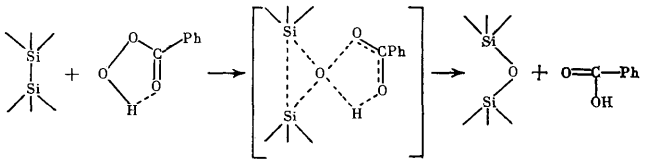
For the tri- and tetrafluorodisilanes, the free-radical direction may make a contribution. Pentamethyldisilane is oxidised by BTMSP more rapidly than hexamethyldisilane, to give a

mixture of products.

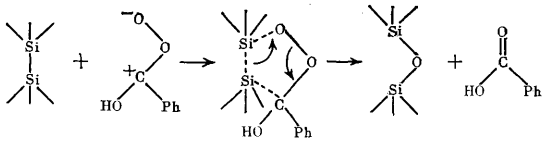
$$Me_5Si_2H + Me_3SiOOSiMe_3 \rightarrow (Me_3SiO)_2SiMe_2 + Me_5Si_2OSiMe_3 + (Me_5Si_2)_2O + (Me_3SiOSiMe_2)_2O + (Me_3Si)_2O + H_2O$$

j) Reactions with peroxyacids

Hexamethyldisilane, 1,2-diphenyltetramethyldisilane, and the disilanes $XC_6H_4Si_2Me_5$ (X = H, Me, MeO, Cl) are oxidised by peroxybenzoic acid in dichloromethane or benzene to the corresponding siloxanes.[141] The reactions obey a kinetic equation of second order, first order with respect to each reagent. The satisfactory correlation between lg $k$ and $\sigma^+$ gives for the reaction constant the value $\rho = -0.29$, which characterises the disilane and the peroxyacid as nucleophilic and electrophilic reagents respectively. The author cited proposed a mechanism analogous to that of the epoxidation of alkenes, including electrophilic attack and the insertion of an oxygen atom of the peroxyacid at the Si–Si bond.



A bipolar 1,3-addition mechanism, analogous to that of the epoxidation of alkenes in strongly polar solvents, has also been proposed.[9]



It might have been expected that disilanes having electronegative substituents (Cl, Br, OR, OCOR) on the silicon atoms would be oxidised by peroxybenzoic acid more slowly than the peralkylated compounds. It was found, however, that these compounds react more rapidly than hexamethyldisilane.[142–144] The reactions are of first order with respect to each reagent, and give as the only products the corresponding disiloxanes and benzoic acid.

$$XMe_2SiSiMe_2Y + PhCO_3H \xrightarrow[\text{hexane}]{20^\circ C} XMe_2SiOSiMe_2Y + PhCOOH$$

| X | Y | $k$, litre mole$^{-1}$min$^{-1}$ | X | Y | $k$, litre mole$^{-1}$min$^{-1}$ |
|---|---|---|---|---|---|
| Me | Me | 0.008 | $Me_3Si$ | Cl | 0.42 |
| Me | n-Bu | 0.006 | $Me_3Si$ | $OSiMe_2Cl$ | 0.06 |
| Me | Cl | 0.28 | Cl | Cl | 0.15 |
| n-Bu | Cl | 0.15 | Me | OCOPh | 0.20 |
| Ph | Cl | 0.09 | Me | OEt | 0.06 |

The increased reactivity is evidently due to the existence of $n,\sigma$-conjugation in disilanes having $n$-donor substituents on the silicon atoms. Effects of this kind raise the HOMO of the polysilene,[71] and this should be revealed by an increase in its nucleophilic activity towards soft electrophiles, and in particular towards peroxybenzoic acid. As a result of the combined influence of the $Me_3Si$ group and the $n$-donor substituent in 1-chloroheptamethyltrisilane, only the Si–Si bond adjacent to the chlorine atom reacts initially. Cleavage of the second bond takes place much more slowly ($k_1/k_2 = 7$).[142]

$$Me_3SiSiMe_2SiMe_2Cl + PhCO_3H \xrightarrow{k_1} Me_3SiSiMe_2OSiMe_2Cl + PhCOOH$$
$$Me_3SiSiMe_2OSiMe_2Cl + PhCO_3H \xrightarrow{k_2} Me_3SiOSiMe_2OSiMe_2Cl + PhCOOH$$

The influence of the dielectric constant and basic strength of the solvent on the rate of the oxidation of pentamethylchlorodisilane by peroxybenzoic acid is extremely slight.[143] This agrees with the low absolute values of the Hammett ($\rho = -0.29$)[141] and Taft ($\rho = -0.56$) reaction constants,[143] which indicate that the intermediate state of the system in the oxidation is weakly polar.

Vinylpentamethyldisilane (I) can be converted quantitatively into the epoxydisiloxane (II) by treating with peroxyacids.[141]

$$Me_5Si_2\text{–}CH{=}CH_2 + 2PhCO_3H \xrightarrow[24\,CH]{CH_2Cl_2,20^\circ C} Me_3SiOSiMe_2\text{–}CH(O)CH_2 + 2PhCOOH$$
(I) (II)

At an equimolar reagent ratio, the chief product (79%) is the disilanyl epoxide (III).[145]

$$(I) + RCO_3H \rightarrow Me_5Si_2\text{–}CH(O)CH_2 + (II) + Me_3SiOSiMe_2\text{–}CH{=}CH_2 + RCOOH$$
(III)

The reaction takes place in stages, and in the first stage the vinyl group is oxidised preferentially. The relative rates of oxidation of the C=C bond in $Me_3SiOSiMe_2Vin$, $Me_3SiVin$, and $Me_5Si_2Vin$ are 1.0, 2.1, and 5.6 respectively. Thus the $Me_5Si_2$ group shows stronger donor properties than the $Me_3Si$ and $Me_3SiOSiMe_2$ fragments. *m*-Chloroperoxybenzoic acid (MCPBA) reacts with allylpentamethyldisilane[145] according to the equation:

$$Me_5Si_2\text{–}CH_2CH{=}CH_2 \xrightarrow{MCPBA} Me_3SiOSiMe_2\text{–}CH_2CH{=}CH_2 +$$
$$+ Me_3SiSiMe_2\text{–}CH(O)CH_2 \xrightarrow{H^+} Me_3SiSiMe_2CH_2CH_2C(=O)H$$

k) Reactions with benzoyl peroxide and di-t-butyl peroxide

The reactions of hexamethyldisilane,[146,147] hexaethyldisilane,[148] and pentamethylchlorodisilane[149] with di-t-butyl and benzoyl peroxides take place only at the temperatures of the decomposition of the peroxides to free radicals. In the reactions of hexamethyl- and hexaethyldisilanes, the Si–Si bond is not split by the peroxide compounds or the radicals formed by their thermal decomposition. The reaction of pentamethylchlorodisilane with di-t-butyl peroxide is accompanied by the formation of siloxane products, but the latter are obtained as a result of secondary reactions of $Me_5Si_2Cl$ with t-butyl alcohol and not with the peroxide or its radicals. The reaction of pentamethylchlorodisilane with benzoyl peroxide gives a complex mixture of products as a result of radical and exchange reactions.[149]

$$Me_5Si_2Cl \xrightarrow[80-90^\circ C]{(PhCOO)_2} Me_3SiCl + Me_2SiCl_2 + Me_2SiOCOPh + Me_5Si_2OCOPh + PhCOOH + \text{polymer}$$

The free-radical reactions of organopolysilanes with peroxides have been reviewed,[150] and are used for preparative purposes.[9,17]

l) Reactions with t-butyl hydroperoxide and its derivatives

In Ref. 151, an attempt was made to obtain two peroxides with a silicon–silicon bond in the molecule by the reaction of pentamethylchlorodisilane (IV) and 1,2-dichlorotetramethyldisilane (VII) with t-butyl hydroperoxide (TBHP) in the presence of pyridine. Instead of the compounds

expected, the authors cited obtained t-butoxypentamethyldisiloxane (VI) and the siloxane peroxide (X), whose formation was attributed to successive substitution and rearrangement:

$$\underset{(IV)}{Me_3Si_2Cl} + Me_3COOH \xrightarrow[-C_5H_5N\cdot HCl]{C_5H_5N} \underset{(V)}{Me_3SiSiMe_2OOCMe_3} \xrightarrow{O} \underset{(VI)}{Me_3SiOSiMe_2OCMe_3}$$

$$\underset{(VII)}{ClMe_2SiSiMe_2Cl} + Me_3COOH \xrightarrow[-C_5H_5N\cdot HCl]{C_5H_5N} \underset{(VIII)}{ClMe_2SiSiMe_2OOCMe_3} \xrightarrow{O}$$

$$\xrightarrow{O} \underset{(IX)}{ClMe_2SiOSiMe_2OCMe_3} \xrightarrow[-C_5H_5N\cdot HCl]{Me_3COOH/C_5H_5N} \underset{(X)}{Me_3COOMe_2SiOSiMe_2OCMe_3} .$$

It was subsequently established,[152] however, that the reaction of equimolar quantities of compound (IV) and TBHP, in addition to compound (VI), gives t-butylperoxypentamethyldisiloxane (XII) in up to 20% yield, which increases to 65% when a two-fold excess of TBHP is used. When the reaction is carried out not with TBHP but with its lithium salt, the yield of compound (XII) increases to 80%. The reaction begins not with the replacement of the chlorine atom but with the oxidation of the Si–Si bond in compound (IV):

$$\begin{gathered} \underset{(IV)}{Me_3Si_2Cl} + Me_3COOLi \rightarrow \underset{(XI)}{Me_3SiOSiMe_2Cl} + Me_3COLi \\ (XI) + Me_3COOLi \rightarrow \underset{(XII)}{Me_3SiOSiMe_2OOCMe_3} + LiCl \\ (XI) + Me_3COLi \rightarrow \underset{(VI)}{Me_3SiOSiMe_2OCMe_3} + LiCl \quad . \end{gathered}$$

Analogous reactions with $Me_3COOLi$ are undergone by the disilanes $RMe_2SiSiMeR'Cl$, where R and R' = Me, Ph, Bu, $Me_3SiO$.[153,154] Pentamethylchlorodisilane is not reactive towards nucleophilic reagents, so that the peroxide (V) is not formed.[143,152]

Compound (VII), 1,2-dichlorotetramethyldisilane, has a greater tendency to undergo nucleophilic substitution, compared with pentamethylchlorodisilane,[143,153] so that the reaction of compound (VII) with TBHP and its lithium salt begins with the replacement of one of the chlorine atoms by an $Me_3COO$ group, with subsequent rearrangement of the peroxide (VIII) to 1-chloro-3-t-butoxytetramethyldisiloxane (IX) (see above). The reaction is complicated by the parallel oxidation of the Si–Si bond in compound (VII) and the subsequent transformation of the siloxanes (XIII) and (XIV) formed:

$$\underset{(VII)}{ClMe_2SiSiMe_2Cl} \xrightarrow[-Me_3COLi]{Me_3COOLi} \underset{(XIII)}{ClMe_2SiOSiMe_2Cl} \rightarrow$$

$$\xrightarrow[-LiCl]{Me_3COOLi} \underset{(XIV)}{Me_3COOMe_2SiOSiMe_2Cl} \xrightarrow[-LiCl]{Me_3COOLi} Me_3COOMe_2SiOSiMe_2OOCMe_3 .$$

The driving force of the rearrangement of the disilanyl peroxide (VIII) is evidently the transformation of the unstable structure Si–Si–O–O into the thermodynamically more stable state with three strong Si–O bonds. A calculation based on the bond energies[155] shows that the gain in energy in the rearrangement is 99 kcal $mole^{-1}$.

The reactions of 1- and 2-chloroheptamethyltrisilanes with $Me_3COOLi$ are multistage successive and parallel processes, beginning with the oxidation of one Si–Si bond.[154] In 1-chloroheptamethyltrisilane (XV), the disilanyl fragment joined to the chlorine atom is oxidised first.

$$\begin{gathered} \underset{(XV)}{Me_3SiSiMe_2SiMe_2Cl} + Me_3COOLi \rightarrow Me_3SiSiMe_2OSiMe_2Cl + Me_3COLi \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (XVI) \\ (XVI) + Me_3COOLi \rightarrow \underset{(XVII)}{Me_3SiSiMe_2OSiMe_2OOCMe_3} + LiCl \\ (XVI) + Me_3COLi \rightarrow \underset{(XVIII)}{Me_3SiSiMe_2OSiMe_2OCMe_3} + LiCl \\ (XVII) + Me_3COOLi \rightarrow Me_3SiOSiMe_2OSiMe_2OOCMe_3 + Me_3COLi \\ (XVIII) + Me_3COOLi \rightarrow Me_3SiOSiMe_2OSiMe_2OCMe_3 + Me_3COLi \end{gathered}$$

The yield of the peroxide (XVII), containing an Si–Si bond in the molecule, reaches 75% when the reaction is carried out with a three-fold excess of $Me_3COOLi$.

The reaction of the organochloropolysilanes $RMe_2SiSiMe_2Cl$ (R = Me, n-Bu, $Me_3Si$) with lithium t-butyl peroxycarbonate[144] takes place in two directions. The first involves the formation of the unstable peroxycarbonate (XIX), which liberates $CO_2$ to give the disilanyl peroxide (XX); the latter undergoes rearrangement to the t-butoxysiloxane (XXI):

$$RMe_2SiSiMe_2Cl + Me_3COOC(O)OLi \rightarrow \underset{(XIX)}{RMe_2SiSiMe_2OC(O)OOCMe_3} + LiCl$$

$$(XIX) \xrightarrow{-CO_2} \underset{(XX)}{RMe_2SiSiMe_2OOCMe_3} \xrightarrow{O} \underset{(XXI)}{RMe_2SiOSiMe_2OCMe_3} .$$

The second direction involves the oxidation of the Si–Si bond by the peroxycarbonate and the subsequent transformations of the chlorodisiloxane (XXII) formed.

$$RMe_2SiSiMe_2Cl \xrightarrow[-Me_3COC(O)OLi]{Me_3COOC(O)OLi} \underset{(XXII)}{RMe_2SiOSiMe_2Cl} \rightarrow$$

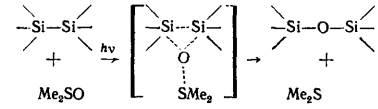
$$\xrightarrow[-LiCl]{Me_3COOC(O)OLi} RMe_2SiOSiMe_2OC(O)OOCMe_3 \xrightarrow{-CO_2} RMe_2SiOSiMe_2OOCMe_3$$

m) Photolytic reactions of organopolysilanes in the presence of oxygen-containing reagents

The photolysis of organopolysilanes in the presence of alcohols, ketones, and other organic compounds containing one or several oxygen atoms in the molecule gives products containing the fragments Si–O–Si and Si–O–C.[12,13,140,156–166] Reactions of this type involve several stages, and take place with the initial formation of silylenes, which undergo subsequent transformations to give the final siloxane products. For example, the irradiation of a mixture of dodecamethylcyclohexasilane and dimethyl sulphoxide (DMSO) gives dimethylsilylene, which is then oxidised by DMSO to dimethylsilanone. The latter, in the absence of reagents which act as traps, undergoes oligomerisation.[162]

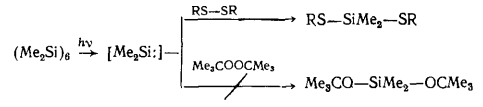
$$(Me_2Si)_6 \xrightarrow{h\nu} [Me_2Si:] \xrightarrow{Me_2SO} [Me_2Si{=}O] \rightarrow (Me_2SiO)_n$$

In the photolysis of pentamethylphenyldisilane, 2-phenylheptamethyltrisilane, and other aryl-substituted polysilanes in the presence of DMSO, one of the directions of the reaction involves the oxidation of the photo-excited Si–Si bond by dimethyl sulphoxide to give the corresponding siloxanes.[140,161,163,164]




Dimethylsilylene is introduced at the S–S bond of the

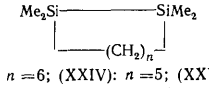
disulphides. The corresponding reaction with di-t-butyl peroxide does not take place.[165]



## 2. Oxidation of Cyclic Organopolysilanes

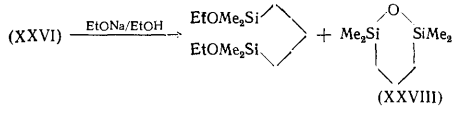
### a) The influence of ring size on reactivity

The organopolysilane ring size is one of the important factors determining the reactivity of these compounds in oxidative cleavage. The reactivity of the Si–Si bond is also influenced strongly by the size of the substituents on the silicon atoms and the nature of the heteroatoms in the ring. The increase in reactivity with decrease in ring size can be followed in the series of tetramethyl-1,2-disilacycloalkanes (XXIII)–(XXVII).[167]



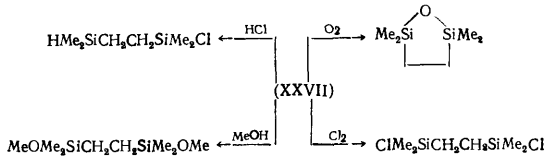
(XXIII): $n=6$; (XXIV): $n=5$; (XXV): $n=4$; (XXVI): $n=3$, (XXVII): $n=2$

In these compounds, the influence of internal angular strain on the reactivity of the Si–Si bond begins to appear in the six-membered ring of compound (XXV). The action of sulphuric acid on disilacyclo-octane (XXIII) and disilacycloheptane (XXIV), as in the case of hexamethyldisilane, does not split the Si–Si bond, and the methyl group is replaced, whereas the reactions of compounds (XXV) and (XXVI) with concentrated sulphuric acid lead to cleavage of the Si–Si bond. The greater angular strain in compound (XXVI), compared with compound (XXV), is revealed in the reactions with oxygen, bis(trimethylsilyl) peroxide,[107] and sodium ethoxide.[157] 1,2-Disilacyclohexane (XXV) does not react with oxygen, whereas 1,2-disilacyclopentane (XXVI) absorbs oxygen exothermally, and is converted into the corresponding siloxane derivative (XXVIII). The reaction of compound (XXV) with BTMSP takes place only on heating to 50 °C, whereas compound (XXVI) reacts readily even at 20 °C. The silicon–silicon bond in compound (XXV) is not split by a solution of sodium ethoxide in ethanol at 90 °C, whereas in compound (XXVI), quantitative cleavage of the Si–Si bond takes place:



(XXVIII)

With further decrease in the ring size there is a sharp increase in the reactivity of the disilacycloalkane. 1,1,2,2-Tetramethyl-1,2-disilacyclobutane (XXVII) is extremely reactive.[168] It can be kept for a long time only at liquid nitrogen temperature. At 20 °C, the polymer $-(-CH_2CH_2.SiMe_2SiMe_2-)_n-$ is formed. The reactions of compound (XXVII) with oxygen, chlorine, hydrogen chloride, and methanol take place very vigorously.



A decrease in the reactivity of the Si–Si bond with increase in ring size was also observed[169] in the reactions of the 1,2-disilacycloalkanes (XXIV)–(XXVI) with *m*-chloroperoxybenzoic acid. The relationship between the kinetic parameters of the oxidation and the energies of charge transfer ($E_{ct}$) in the disilane–tetracyanoethylene complexes was studied. On going from the linear hexamethyldisilane to 1,2-disilacyclopentane (XXVI), the reaction rate constant increases by a factor of 2000. The entropy of activation remains practically constant, and the enthalpy of activation decreases. With decrease in the ring size, $E_{ct}$ decreases regularly, indicating that the HOMO level of the disilacycloalkane is raised, probably as a result of strain in the ring. The observed linear relationship between the enthalpy of activation and the energy of charge transfer indicated that in the transition state of the reaction, an important role is played by electronic donor–acceptor interaction between the disilane (donor) and the peroxyacid (acceptor).

The data on the oxidative splitting of organocyclopolysilanes, given below, also show that the reactivity of these compounds increases with decrease in the ring size.

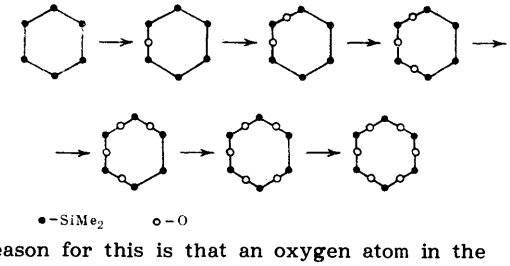
### b) The oxidation of six-membered cyclic compounds containing silicon–silicon bonds

A fairly large number of varied six-membered cyclic compounds containing from one to six Si–Si bonds in the molecule are now known. In addition to disilanyl fragments, the ring may contain

$-(CR_2-)_n-$, $-CR=CR-$, $\diagdown C=PR_3$, $-NH-$, $-NR-$ $\diagdown N-NH_2$, $\diagup$

$-O-SO_2-O-$, etc. groups, and also elements such as oxygen and sulphur.[1,2,7,9,17,18,21,22] Most of these compounds are inert towards atmospheric oxygen at room temperature. The instability of some of them[52,170,171] in air may be due to the presence in the ring of a phosphorus-containing ligand such as $\diagdown P-Ph$.
$\diagup$

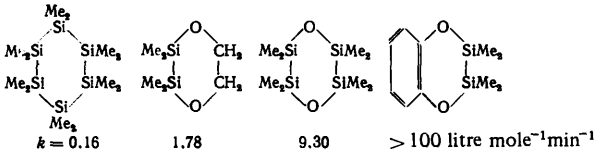
The six-membered ring $(Me_2Si)_6$ is the most stable thermodynamically. The equilibrium in a mixture of the compounds $(Me_2Si)_n$ ($n$ = 5, 6, 7) in the presence of Na/K alloy is displaced towards the formation of dodecamethylcyclohexasilane.[172] The latter undergoes practically no oxidation by atmospheric oxygen and 30% hydrogen peroxide solution at 80 °C. Chromium oxide, potassium dichromate, and potassium permanganate oxidise dodecamethylcyclohexasilane to a complex mixture of siloxane products.[173] MCPBA splits all six Si–Si bonds in $(Me_2Si)_6$, and each successive oxygen is introduced into the bond adjacent to that already oxidised.[174]



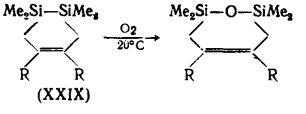
•–$SiMe_2$ o–O

The reason for this is that an oxygen atom in the $-(-\overset{|}{\underset{|}{Si}}-)_n-$ chain activates the neighbouring Si–Si bond towards oxidation by peroxyacids. The first stage is the slowest, so that the intermediate oxygen-containing rings formed do not accumulate to significant concentration in the

reaction mixture. Comparison of the rate constants for the reactions of various six-membered rings with peroxybenzoic acid (benzene, 35 °C)[144] shows the magnitude of the activating influence of oxygen (particularly when combined with the π-system of the benzene ring[159]) on the Si–Si bond being oxidised.

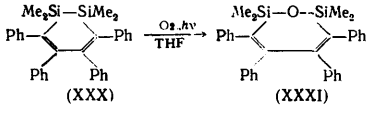



The presence of one multiple bond in the six-membered silicon–carbon ring of compound (XXIX) increases its ability to be oxidised by oxygen, compared with 1,2-disilacyclohexane (XXV).[157–177]



(XXIX)

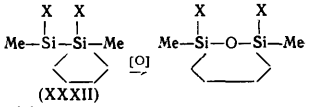
The cyclodisilane (XXX), which contains a diene group, is not oxidised by oxygen in acetone under the influence of light and in the presence of a sensitiser, but the reaction takes place readily in tetrahydrofuran (THF). MCPBA converts compound (XXX) quantitatively into the cyclodisiloxane (XXXI) at 20 °C.



(XXX) (XXXI)

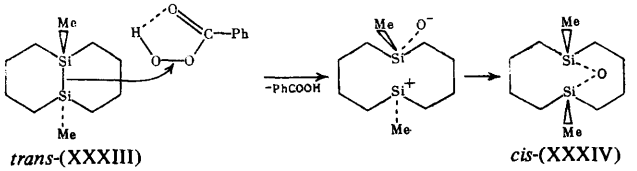
The reactions with di-t-butyl peroxide and t-butyl hydroperoxide take place only at 60–100 °C.[178]

The reactions of the stereoisomeric 1,2-disilacycloalkanes (XXXIIa,b) with peroxybenzoic acid or bis(trimethylsilyl) peroxide take place with preservation of the configuration, indicating that the oxidation takes place by a molecular mechanism.[179,180]



(XXXII)
(a) X=F;
(b) X=Ph.

In the reactions of *trans*-9,10-dimethyl-9,10-disiladecaline (XXXIII) with $PhCO_3H$ and $Me_3SiOOSiMe_3$, inversion of the configuration is observed, due to the fact that the *trans*-isomeric siloxane oxidation product has considerable strain, whereas the *cis*-isomer (XXXIV) is unstrained. In the opinion of the authors cited, the inversion takes place at the moment of electrophilic attack by the peroxide on the Si–Si bond.[181,182]

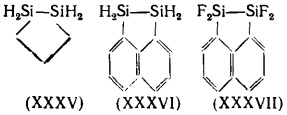


*trans*-(XXXIII) *cis*-(XXXIV)

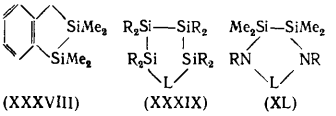
c) The oxidation of five-membered cyclic compounds containing Si–Si bonds

Five-membered silicon or silicon–carbon rings containing Si–Si bonds are more strained than six-membered rings. This is revealed by the slightly higher reactivity of these compounds towards oxygen and other oxidising agents. Dodecamethylcyclohexasilane does not react with atmospheric oxygen, whereas decamethylcyclopentasilane is slowly oxidised in air.[183,184] Compounds with more bulky substituents on the silicon, such as decaphenyl- and decaethylcyclopentasilanes, however, do not react with atmospheric oxygen.[1,185] The cleavage of decamethylcyclopentasilane by chlorine is much more rapid than that of dodecamethylcyclohexasilane.[125] Sulphur or selenium are inserted into the polysilicon ring $(Me_2Si)_5$ at 190 °C.[186] Dodecamethylcyclohexasilane does not react with sulphur and selenium under analogous conditions.

1,2-Disilacyclopentane (XXXV) was found to be extremely reactive towards $O_2$, probably due to not only the deformation of the Si–Si bond but also the presence in the molecule of easily oxidised Si–H bonds. In contrast to this, the Si–Si and Si–H bonds in 1,2-disila-acenaphthene (XXXVI) are stable to atmospheric oxygen.[187] It was previously noted that fluorodisilanes with a linear or cyclic structure, containing two or more fluorine atoms on silicon, are rapidly oxidised in air.


(XXXV) (XXXVI) (XXXVII)

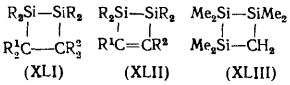
The disila-acenaphthene (XXXVII), however, whose molecule contains four fluorine atoms, was found to be stable to oxygen.[187] 1,1,2,2-Tetramethyl-1,2-disila-4,5-benzocyclopentene (XXXVIII) reacts under mild conditions with MCPBA and oxygen to give the corresponding siloxane. The higher rate of oxidation of this compound compared with pentamethylphenyldisilane has been noted.[188]


(XXXVIII) (XXXIX) (XL)

The introduction of the heteroelement into the ring alters the sensitivity of the product to oxygen. For example, compounds with the general formula (XXXIX) with R = Me, Ph and L = O, NH, NR are stable in air. The boron- and phosphorus-containing heterocycles with L = $BNMe_2$, PPh[52,170,189] were found to be very sensitive to oxygen and moisture. In all known five-membered heterocycles with the general formula (XL),[190,191] the Si–Si bond remains inert to $O_2$. In the phosphorus-containing heterocycles, the heteroelement is oxidised.[190]

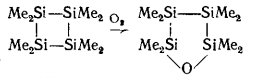
d) The oxidation of four-membered cyclic compounds

The even greater angular strains of the Si–Si, Si–C and C–C bonds in di- and trisilacyclobutanes (XLI), (XLIII), disilacyclobutenes (XLII), and cyclotetrasilanes $(R_2Si)_4$ lead to a further increase in the reactivity of these compounds. The tetrafluorodisilacyclobutenes (XLII) (R = F, $R^1$ and $R^2$ = H, Me, Et, $Me_3C$)[192] and 1,1,2,2,3,3-hexamethyl-1,2,3-trisilacyclobutane (XLIII)[193] are thermally unstable, and rapidly oxidised in air.


(XLI) (XLII) (XLIII)

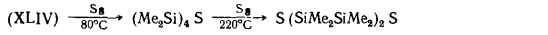
The disilacyclobutanes (XLI) and disilacyclobutenes (XLII) with methyl substituents on the silicon atoms[194,198] are fairly stable to heat, but are very sensitive to oxygen, and are oxidised in solution to the corresponding siloxanes. The aryl-substituted compounds (XLI) (R = phenyl, *m*- or *p*-tolyl) are stable to atmospheric oxygen, but are transformed into siloxanes by the action of MCPBA.[199,200]

Octamethylcyclotetrasilane (XLIV) is very reactive towards oxygen. The formation of small quantities of this compound in the reaction of dimethyldichlorosilane with sodium–potassium alloy in THF has been assumed.[201] In spite of the precautions taken, the authors cited could not isolate this compound from the reaction mixture, because of its rapid oxidation by even traces of oxygen. Kumada and co-workers[202,203] obtained compound (XLIV) by the photolysis of a cyclohexane solution of dodecamethylcyclohexasilane in a nitrogen atmosphere. It was impossible to avoid partial oxidation of compound (XLIV) to the monoxide (XLV) during the reaction and the isolation of the product.

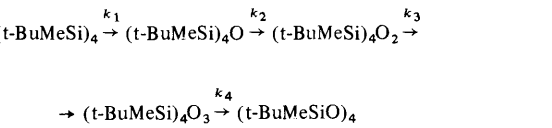


(XLIV) (XLV)

1,2,3,4-Tetraethyltetramethylcyclotetrasilane is also unstable in air.[204] Sulphur or selenium are inserted at the Si–Si bonds of octamethylcyclotetrasilane to give five-membered and symmetrical six-membered rings.[205,206]

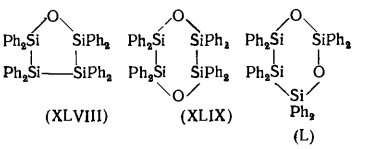


1,2,3,4-Tetra-t-butyltetramethylcyclotetrasilane (XLVI), prepared by West and co-workers,[207] showed a number of unexpected properties, namely the lowest first ionisation potential of all known polysilanes (7.42 eV, PES) and the maximum long-wave ultraviolet absorption (300 nm),[51,208,209] indicating that the energies of the ground and the first excited states differ little. The silicon–silicon bond length (2.377 Å) is greater than the known values for permethylated cyclopolysilanes (2.338 Å for dodecamethylcyclohexasilane). It should be expected that in the strained four-membered ring of compound (XLVI), the strongly deformed silicon–silicon bond with a low value for the first ionisation potential would readily be split by oxidising reagents. It was found, however, that this compound is stable to oxygen and warm concentrated sulphuric acid. The unusual chemical inertness of compound (XLVI) is attributed to the steric effects of the bulky t-butyl groups.[210] All four isomers of $(t\text{-BuMeSi})_4$ are oxidised by MCBPA, but at different rates.[211]



The oxygen atom in the ring is activated towards oxygen by the neighbouring Si–Si bonds, but the ring strain still predominates, so that $k_1 > k_2 > k_3$. The Si–Si bond between the *cis*-substituents is most easily oxidised. The triply-oxidised product $(t\text{-BuMeSi})_4O_3$ does not accumulate in the reaction mixture, but is rapidly oxidised to the tetrasiloxane ($k_4 \gg k_3$).

Perphenylated cyclotetrasilane $(Ph_2Si)_4$ (XLVII), which is thermally stable, is slowly oxidised by atmospheric oxygen to give octaphenoxytetrasilacyclopentane (XLVIII) and a siloxane polymer.[1,2]



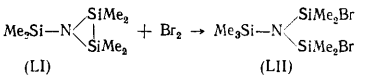
(XLVIII) (XLIX) (L)

Octaphenylcyclotetrasilane is oxidised by atmospheric oxygen in toluene at 100 °C and by ozone in $CCl_4$ or carbon disulphide. Compounds (XLVIII) and (XLIX) were isolated from the products of these reactions.[1,2] Nitrobenzene reacts with compound (XLVII) to give as main product the 1,3-dioxide (L). Benzaldehyde oxidises compound (XLVII) rapidly, whereas benzyl alcohol, acetophenone, paraldehyde, and pentyl nitrite react slowly. The products of these reactions are the monoxide (XLVIII), the 1,4-dioxide (XLIX), and a polymer.[1,2] The silicon–silicon bond in octaphenylcyclotetrasilane is readily split by halogens, hydrogen halides, mercury halides and acetate, tin(IV) chloride, phosphorus(V) chloride, and various organic halogeno-compounds. Decaphenylcyclopentasilane is more stable to these reagents, and cleavage requires more severe conditions.[1,2,17,212,213]

Thus four-membered cyclic compounds containing from one to four Si–Si bonds in the ring have different thermal stabilities, but practically all are fairly sensitive to oxidising agents, and cleavage of the Si–Si bonds, and not the Si–C, C–C, or C=C bonds, always takes place. Bulky substituents have an appreciable stabilising influence on the cyclosilane molecule.[214,215]

e) The oxidation of three-membered rings

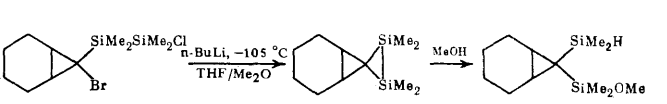
The first three-membered ring with an Si–Si bond in the molecule, namely N-trimethylsilyltetramethylcyclodisilazane (LI), was obtained in 1963;[216] it is thermally stable, and is not oxidised in air. Prolonged boiling of compound (LI) in a solution of alkali in hexanol leads to only partial cleavage of the Si–Si bond. On the other hand, the reaction with bromine in $CCl_4$ takes place readily to give the dibromo-derivative (LII).



(LI) (LII)

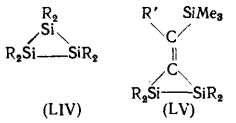
Compound (LI) is slowly hydrolysed by water to give ammonia and siloxanes. Its low reactivity may indicate that there is very little or no deformation of the Si–Si bond.

Disilacyclopropane (LIII), synthesised in 1976, exists only at temperatures below −100 °C. As expected, the most reactive bond in this compound is not the Si–C but the Si–Si bond, which is split by methanol at −105 °C.[217]



(LIII)

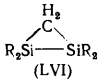
The subsequent search for methods of synthesising silicon-containing rings[80–86,218–221] gave a number of di- and trisilacyclopropane systems (LIV)–(LVI), which were found to be completely stable to heat and fairly inert towards oxygen or moisture.



(LIV) (LV)

R = 2,6-dimethylphenyl (a) (Ref.80), neopentyl (b) (Ref.85), t-butyl (c) (Ref.219), 1-ethylpropyl (d) (Ref.81), isopropyl (e) (Refs.81, 86)

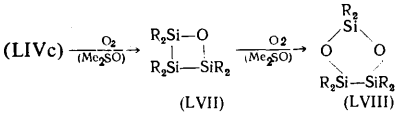
R = mesityl, R′ = trimethylsilyl (a) or phenyl (b) (Ref.218)



(LVI)

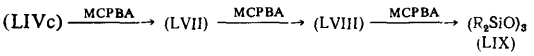
R = 2,6-dimethylphenyl (Ref.82)

An exception is hexaisopropylcyclotrisilane (LIVe), which decomposes slowly when kept, and reacts rapidly with atmospheric oxygen.[81,86] Hexa(2,6-dimethylphenyl)-cyclotrisilane (LIVa) is readily split by chlorine.[80] Hexa-t-butylcyclotrisilane (LIVc) in toluene is oxidised very slowly by atmospheric oxygen to the mono- and dioxa-derivatives (LVII) and (LVIII). The reaction with dimethyl sulphoxide in boiling toluene is similar.



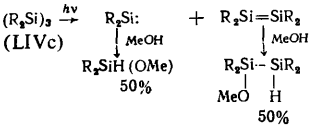
(LVII) (LVIII)

MCPBA successively splits all three silicon–silicon bonds in compound (LIVc) at room temperature, the final product being hexa-t-butylcyclotrisiloxane (LIX).

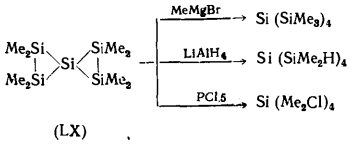


(LIX)

Sulphur and selenium are inserted at the Si–Si bond of hexa-t-butylcyclotrisilane in boiling toluene to give the four-membered rings $(R_2Si)_3Z$ (Z = S, Se).[220] The reaction of compound (LIVc) with methanol with irradiation by ultraviolet light takes place with the intermediate formation of di-t-butylsilylene and tetra-t-butyldisilene.[219]



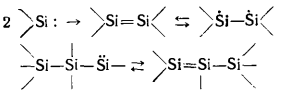
The disilacyclopropanes (LVa, b) do not react with alcohols at room temperature.[218] Compounds (LIVd) and (LVI) are oxidised to the corresponding mono-oxa-derivatives by atmospheric oxygen[81] or MCPBA.[82] The high thermal stability and low chemical activity of the silacyclopropanes (LIVa–d), (LV), and (LVI) is attributed to the steric shielding of the silicon atoms by the bulky substituents. According to Ref.221, unexpected thermal stability is shown by octamethylspiropentasilane (LX), which has practically no stabilising bulky substituents on the silicon atoms. Its chemical activity is fairly high, however.



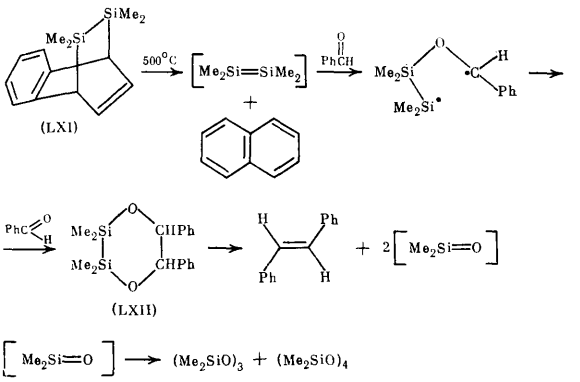
(LX)

## V. THE OXIDATIVE CLEAVAGE OF THE SILICON–SILICON DOUBLE BOND

The formation of disilene as a short-lived intermediate compound in the thermal decomposition of benzo-7,8-disilabicyclo[2,2,2]-octa-2,5-dienes, for example compound (LXI), was first postulated in 1972.[222] It was subsequently shown that disilene intermediates[223] may be obtained by the dimerisation[224,225] and rearrangement[226,227] of silylenes.



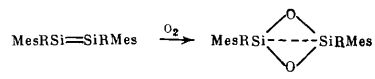
These highly active species behave as disilenes[228] or as biradicals,[229–231] depending on the substituents on silicon and on the reaction conditions. Disilenes undergo cycloaddition with dienes,[232,233] and dimerise to cyclotetrasilanes;[234,235] the reactions with oxygen-containing compounds[233,236] give products with Si–O bonds. For example, tetramethyldisilene, obtained by decomposing compound (LXI), reacts with benzaldehyde to give hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, and trans-stilbene.[236] The proposed scheme includes the formation of radical and silanone intermediates.



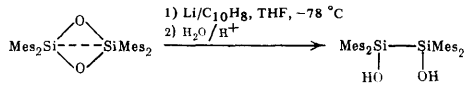
(LXI) (LXII)

Evidence in support of this scheme is provided by the fact that 1,2-disila-3,5-dioxacyclohexane (LXII), obtained by direct synthesis, decomposes at 500 °C to give the same products.

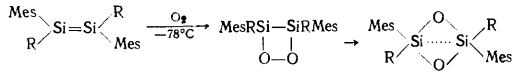
The latest achievements in the synthesis of stable disilenes[24,25,76–88,237–248] have made it possible to investigate their reactivity towards various oxidising reagents under ordinary conditions, that is in solution and at room temperature. The disilenes known at present differ in their thermal stability and reactivity, which are determined by the steric effects of the substituents on the silicon atoms. The mesityl[25,77] 2,6-dimethylphenyl,[80] and 2,6-diethylphenyl[84] groups give fairly stable compounds, which withstand heating for a short time up to the melting points (see Table). Alkyl-substituted disilenes are less stable. Thus the half-decomposition time of tetra-t-butyldisilene at room temperature is 4–10 h;[83,87] tetraisopropyldisilene is even less stable.[86] The disilenes with the highest thermal stability are slightly less active in reactions with oxidising reagents. Overall, the chemical properties of disilenes are similar to those of alkenes, but their activity is appreciably greater. The yellow colour characteristic of disilenes disappears rapidly on contact with air. Oxygen reacts with the powdered disilenes MesRSi=SiRMes [R = Mes (mesityl), $Me_3C$, $(Me_3Si)_2N$] at 25 °C to give the corresponding cyclodisiloxanes.[237]



X-Ray diffraction[238] has shown that in the cyclodisiloxanes, the silicon atoms are situated at a distance shorter than the length of an ordinary silicon–silicon bond. Thus in tetramesitylcyclodisiloxane the Si–Si distance is 2.31 Å, whereas the length of the silicon–silicon bond in 1,1,2,2-tetramesityldisilane is 2.35 Å. Thus bonding is possible between the silicon atoms in cyclodisiloxanes.[238–243] This is confirmed by the reaction of tetramesitylcyclodisiloxane with naphthalene–lithium, which takes place with preservation of the Si–Si bond and gives 1,1,2,2-tetramesityldisilandiol after hydrolysis.[238]

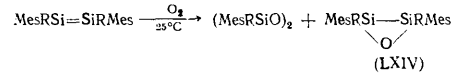


The oxidation of *trans*-dimesityldi-t-butyldisilene by oxygen in solution in pentane or THF at −78 °C gives the disiloxetane (LXIII), which undergoes quantitative rearrangement into *trans*-dimesityl-di-t-butylcyclodisiloxane when the solution is heated to room temperature.[237]



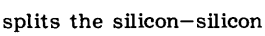
(LXIII)

When the reaction is carried out in pentane at 25 °C, the products are *trans*-dimesityldi-t-butylcyclodisiloxane and the disilanyl epoxide (LXIV).

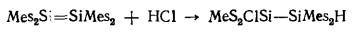


(LXIV)

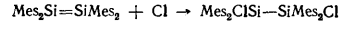
The disilanyl epoxide (LXIV) is stable to oxygen, but it can be converted into the cyclodisiloxane by the action of MCPBA.[237]



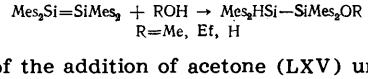
Hydrogen chloride splits the silicon–silicon double bond in tetramesityldisilene to give 1-chloro-2-H-tetramesityldisilane.[25,77]



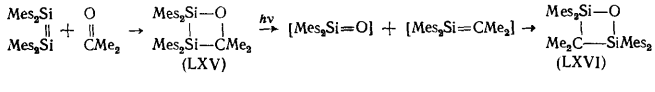
The reaction with chlorine in benzene gives 1,2-dichlorotetramesityldisilane.[77]



If however the reaction is carried out in alkanes, the product is 1-chloro-2-H-tetramesityldisilane, and this was attributed to the radical mechanism.[77] Tetramesityldisilene reacts with alcohols and water at 50 °C,[25,77] and also with carbonyl compounds.[77]

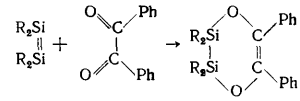


The product of the addition of acetone (LXV) undergoes rearrangement on irradiation to give the 1,3-isomer (LXVI).

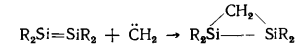


(LXV) (LXVI)

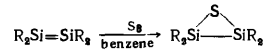
The reactions of tetramesityldisilene[76] and tetra-t-butyldisilene[87] with benzil takes place as [2 + 4]-cyclo-addition.



Carbene is inserted at the silicon–silicon bond to give disilacyclopropane.[82]



The reaction with sulphur gives the episulphide.[237,243]



The reaction of tetra-t-butyldisilene with dienes takes place as [2 + 2]- or [2 + 4]-cyclo-addition.[83,87] Tetramesityldisilene does not react with traditional disilene traps such as anthracene, 2,3-dimethylbutadiene, 1,4-diphenylbutadiene, and phenyl(trimethylsilyl)acetylene, but it undergoes cycloaddition with phenylacetylene.[77]

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The oxidative cleavage of the silicon–silicon bond may take place by free-radical, molecular, or heterocyclic mechanisms, depending on the type of polysilane and oxidising agent. The cleavage may be due to rearrangement of the polysilane, in which the $R_3Si$ group migrates from the silicon atom to a more electronegative element. The silicon–silicon bond acts as the nucleophilic centre in reactions with electrophilic reagents such as peroxyacids and halogens. Cleavage by nucleophilic reagents takes place more readily if the silicon atoms are surrounded by electron-acceptor substituents. The influence of ring size and the size of the substituents on the reactivity of the Si–Si bond can be clearly seen. The reactivity of the silicon–silicon double bond is appreciably greater than that of $\sigma_{Si-Si}$ and $\pi_{C-C}$ bonds.

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# The Nuclear Magnetic Resonance Spectroscopy of $^{15}N$-Labelled Cyclophosphazenes

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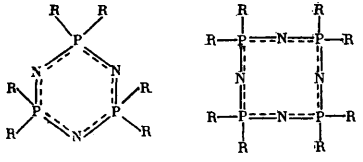
The $^{31}P$ NMR spectra of $^{15}N$-labelled cyclophosphazenes contain additional information compared with the unlabelled compounds, namely, apart from the spin-spin coupling constant $J_{PN}$, it is also possible to obtain information, in the case of homosubstituted compounds, about the spin-spin coupling constants $J_{PP}$ and $J_{NN}$. The $^{15}N$ NMR spectra of these compounds yield the same information and in addition the chemical shift of the $^{15}N$ signal. All these NMR parameters are sensitive to changes in the electronic structure of the cyclic P-N systems, which depend on the type and number of substituents and also on the ring size. Studies on labelled halides, amino-derivatives, ethers, thioethers, and alkyl-substituted derivatives of cyclic phosphazenes containing between three and six P-N structural units are examined. The NMR data are interpreted on the basis of empirical relations and also with the aid of semiempirical quantum-chemical methods.
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## I. INTRODUCTION

Cyclophosphazenes are inorganic cyclic compounds with alternating phosphorus and nitrogen atoms. Their simplest representatives are cyclotriphosphazenes with three $NPR_2$ fragments and cyclotetraphosphazenes with four $NPR_2$ fragments.



The P–N bond length is intermediate between the lengths of single and double bonds. For identical substituents, all the bonds in the ring are likewise identical, i.e. there is no alternation of double and single bonds between the P and N atoms. According to the model of Craig and Paddock,[1] a more or less pronounced cyclic delocalisation of molecular $\pi$ orbitals is postulated, while Dewar et al.[2] suggest that the conjugation terminates at each phosphorus atom (the island model). In addition some workers[3,4,5] have postulated the presence of transannular P–P bonds, which are particularly evident in hexafluorocyclotriphosphazene.

There exist numerous derivatives of cyclophosphazenes differing from one another by ring size and also by the type, number and positions of the substituents R; NMR has proved to be a convenient method for the identification and investigation of these compounds.

The first measurement of the chemical shift of the $^{31}P$ signal in the NMR spectra of cyclophosphazenes was made by Van Wazer et al.[6] in 1956. Among 200 phosphorus compounds investigated, there were also hexachlorocyclotriphosphazene and, in addition, according to the authors, a linear phosphazene. In 1959 Becke-Goehring and Koch[7] used $^{31}P$ NMR to identify cyclophosphazene oligomers and polymers. In the same year $^{31}P$ NMR was also employed to investigate aminocyclotriphosphazenes with different numbers of substituents.[8] The possibility of investigating the NMR spectra of suitable magnetic nuclei forming part of the composition of the substituent R in order to determine the molecular structure of cyclophosphazene as well as their isomers was first reported in 1961. Ray and Shaw studied the $^{1}H$ NMR spectra of dimethylaminocyclotriphosphazenes[9] and Chapman et al.[10] as well as Heffernan and White[11] investigated the $^{19}F$ NMR spectra of trimeric chlorofluoro-derivatives.

In recent years one of the principal methods for the determination of the structures of aminocyclophosphazenes as well as their ethers and thioethers and other phosphazenes with proton-containing substituents has been $^{1}H$ NMR. In order to simplify the spectra, homonuclear decoupling has been used in some cases.[12] This method made it possible to identify unambiguously in many instances the substitution products (the geminal and *cis*- or *trans*-non-geminal positions of the substituents).

The wide-scale use of $^{31}P$ NMR for the determination of the structures of cyclophosphazenes did not begin until the middle 1970s. As an example, one may quote a study[13] on aminophosphazenes. As Fourier transform spectroscopy and the associated possibility of measuring the $^{13}C$ NMR spectra of compounds with the natural abundance of carbon isotopes developed, it became possible to employ this method to investigate cyclophosphazenes with organic substituents.[14-18] Mason et al. published in 1977 a report[19] in which they describe studies of cyclophosphazenes by broad-line $^{14}N$ NMR. Other nuclei forming part of the composition of the P–N rings were first investigated in this way and the nitrogen chemical shifts were measured for certain triphosphazenes and cyclotetraphosphazenes with the same substituents.

In the majority of investigations of cyclic phosphazenes, NMR is used to identify the reaction products or to investigate the structure of the compound synthesised but not in systematic research permitting an interpretation of the NMR parameters. The aim of our studies was to determine, by investigating the NMR spectra of $^{15}N$-labelled cyclophosphazenes, additional parameters which yield much information about these cyclic P–N systems.

Phosphazenes with identical substituents, fully labelled by $^{15}N$, are spin systems of the type AA'A"XX'X" in the case of the trimeric compounds and of the type AA'A"A"'XX'X"X"' in the case of tetrameric compounds, provided that spin–spin coupling with the substituents is absent or is suppressed. The higher-order NMR spectra obtained permit the determination of the following parameters: (1) the chemical shifts $\delta_P$ and $\delta_N$, (2) the coupling constants $^1J_{PN}$ and $^2J_{PP}$, and (3) the coupling constants $^2J_{NN}$ and $^3J_{PN}$. The latter quantities are very small for cyclophosphazenes and are not resolved in the experimental spectra. This is indicated by the results of studies on cyclophosphazenes with mixed substituents.[20–23] The neglect of these coupling constants greatly simplifies the analysis of the spectra. This also applies to the coupling constants $^4J_{PP}$[20,24–26] and $^4J_{NN}$ for the spectra of tetrameric phosphazenes.

The $^{31}P$ and $^{15}N$ NMR spectra of cyclic phosphazenes with identical substituents are symmetrical and the positions of the centres yield information about the chemical shifts (Fig. 1). The coupling constants $^1J_{NN}$ can be obtained from both spectra; the distance between the outer intense lines given by

$$2^1J_{PN}+{}^3J_{PN}$$

is used to determine it. Since $^3J_{PN}$ is negligible, half this distance represents the value of $^1J_{PN}$. In order to obtain the coupling constants $^2J_{PP}$ for cyclotriphosphazenes[27] and cyclotetraphosphazenes[28] we developed graphical methods based on the continuous variation of the distances between the additional spectral lines as a function of the ratio $^2J_{PP}/{}^1J_{PN}$. In this way it is possible to do without the computer modelling for the simulation of the spectra. We may note that analysis of the spectra in such cases does not yield information about the relative signs of the coupling constants.

$^{15}N$-Labelled cyclophosphazenes with mixed substituents also give rise to $^{31}P$ and $^{15}N$ NMR spectra containing high-order lines. In most cases preliminary data can be extracted from these spectra by means of first-order analysis. Modelling of the spectra enables one to refine these estimates.[20,21,23] In some cases it is then possible to determine the relative signs of the coupling constants.

The empirical interpretation of the NMR parameters permits the conclusion that the atoms of the substituents linked directly to phosphorus, i.e. the oxygen atoms in ethers, the nitrogen atoms in amino-derivatives, etc., exert a direct influence on such spectra. Relations are then observed between the NMR parameters and the positions of the corresponding elements in the Periodic System.[29] This simplified treatment is useful also in the interpretation of NMR data with the aid of semiempirical quantum-mechanical calculations for model compounds.[30,31]

It is therefore of interest to investigate how the NMR parameters vary (a) with the substituents R (in the first place one considers substituents of the same type), (b) with ring size (under the same conditions), and (c) with the degree of substitution (when cyclophosphazenes with mixed substituents are considered). Attention will be concentrated in this review on the possibility of obtaining from NMR data information about the characteristics of the P–N bond system in cyclophosphazenes.

## II. THE $^{31}P$ CHEMICAL SHIFTS

The $^{31}P$ NMR chemical shifts have been determined for almost all the hexa-substituted cyclotriphosphazenes synthesised, for example, for R = F,[32–35] Cl[6–8,35–41] etc., Br,[32,35,42,43] NCS,[41,44,45] $N_3$,[46] OMe,[30,39,47] OEt,[30,39,44,47] OPh,[30,39,48,49] SMe,[50] SEt,[37,51] SPh,[20] $NH_2$,[21,32,41] NHMe,[8,13,30] NHEt,[13,30] NHPr-iso,[13] NHPh,[30] $NMe_2$,[8,13,30] $NEt_2$,[13,30] $NC_5H_{10}$,[13] Me,[30,52] and Ph.[41,53,54] This also applies to the octa-substituted cyclotetraphosphazenes with R = F,[32,35] Cl,[7,32,35–37] Br,[32,35,42] NCS,[32,44] OMe,[28,47] OEt,[44] OPh,[28] SEt,[51] NHMe,[13] NHEt,[13,28] NHBu-t,[13] $NMe_2$,[13,28] Me,[28,52] and Ph,[13] to certain decasubstituted cyclopentaphosphazenes with R = F,[55] Cl,[35,36] OMe,[47,55] $NMe_2$,[55] and Me,[52] and to dodecasubstituted cyclohexaphosphazenes with R = Cl,[35,36] OMe,[47,55] and $NMe_2$.[55] Finally we may mention $(NPCl_2)_7$[35,36] and $(NPCl_2)_8$.[36]

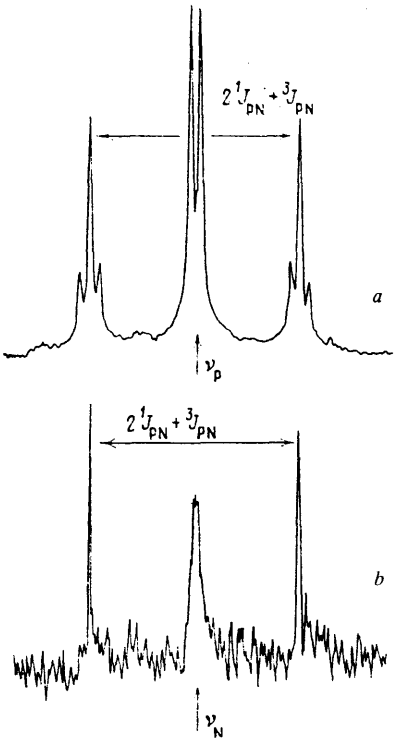



**Figure 1.** Experimental spectra of the compound $(^{15}NPBr_2)_3$: a) $^{31}P$ NMR spectrum; b) $^{15}N$ NMR spectrum.

Table 1 presents the $^{31}P$ chemical shifts for certain identically substituted cyclophosphazenes. The results presented were obtained in our laboratory,[28,30,55] since the available literature data for the chemical shifts had been obtained under different conditions which made it difficult to compare them. For example, it is completely impossible to compare the data[41,45] for the compound $[NP(NCS)_2]_3$ and in other cases the difference between the chemical shifts obtained in different studies for the same compounds reach several p.p.m., for example, for $(NPMe_2)_{3,4}$ (Grushkin et al.[54] and Thomas et al.[28,30]), $[NP(NH_2)_2]_3$ (Moeller[32] and Latscha[41]), $(NPPh_2)_3$ (Reddy and Weis[53] and Grushkin et al.[54]), $[NP(OEt)_2]_3$ (Nielsen et al.[44] and Dhathathreyan et al.[47]), $(NPF_2)_3$ (Allen et al.[33] and Moeller[32]), and $(NPBr_2)_3$ (John and Moeller[42] and Engelhardt et al.[43]). These differences can be understood if one takes into account the fact that the measurements were performed on spectrometers of different degrees

of accuracy and, in addition, for different states of the test substance, for example, without a solvent in the fused state, or after dissolution in various solvents such as water, ether, benzene, $CS_2$, $CH_2Cl_2$, etc. and that the concentration of the test substance also varied within wide limits. Our measurements were performed at 302 K after dissolving the substance in $CDCl_3$; in most cases the concentration of the substance was kept constant (at ~0.5 M) with the sole exception of the $[NP(NH_2)_2]_3$ solution.

In the first major investigation by Van Wazer et al.[6] devoted to phosphorus compounds, which was already mentioned above, the influence of substituents on the $^{31}P$ chemical shift was discussed. The following series of substituents was found for tetracoordinate phosphorus:

$$Se > S > C_{aliph} > C_{arom} \cong P > N \cong Cl > O > F.$$

A similar series was established also for cyclophosphazenes with the exception of $[NP(NHPh)_2]_n$ or $[NP(OPh)_2]_n$, where the phenyl substituent at the nitrogen or oxygen atom influences also the chemical shift of phosphorus.

A qualitative correlation between the electronegativity of the group linked to the phosphorus atom and the $^{31}P$ chemical shift has been established.[40] The electrophilic character of the group R linked to the phosphorus atom is responsible for the partial delocalisation of the free electron pair of the nitrogen atoms in the ring and the formation of additional P–N π-bonds which decreases the chemical shift of phosphorus.

It is seen from the data in Table 1 that the $^{31}P$ chemical shift for cyclophosphazenes with a given ring size diminishes when the substituents are altered in a way corresponding to moving from left to right along the same Period in Mendeleev's Table (from alkylphosphazenes to the fluoro-derivatives and from the thioethers to the chloro-derivatives) and, when substituents belonging to a single Group are varied, $\delta P$ increases on passing from an element in the Second Period to one in the Third Period (from ethers to thioethers and from fluoro-derivatives to chloro-derivatives). Like phosphoryl halides, the bromo-derivatives have very low chemical shifts which has not been explained satisfactorily.

On passing from trimeric to tetrameric phosphazenes with retention of the number and nature of the substituents, $\delta P$ appreciably diminishes, but, on further increase of ring size, the shift decreases more slowly, gradually reaching a limiting value. A decrease of the P–N bond length with increase of ring size corresponds to these changes.[56] This can be explained by the effect which was responsible for the influence of the substituents, i.e. by the more or less effective involvement of the free electron pair of the nitrogen atom in the π-bond system. Thus a correspondence is observed with the results of a quantum-mechanical calculation,[57] according to which there exists a satisfactory correlation between the chemical shifts in the $^{31}P$ NMR spectra of the compounds $(NPCl_2)_n$ (where $n$ = 3, 4, or 5) and the overall overlap of the π-bonds $\Sigma_\pi(PN)$.

The appreciable difference between the $^{31}P$ chemical shifts, and, as will be shown below, between other NMR parameters for cyclotriphosphazenes and cyclotetraphosphazenes is in our view caused by the difference between the molecular geometries. Whereas cyclotriphosphazenes have a virtually planar ring structure, higher oligomers consist of non-planar rings. This unusual structure of cyclotriphosphazenes is reflected in other properties of these compounds, for example, in their dipole moments,[58] which is manifested in its turn by the corresponding behaviour in the chromatographic separation of the test substance.[29,59]

For a more detailed interpretation of the relation between the $\delta P$, $\delta N$, $^1J_{PN}$, and $^2J_{PP}$ parameters of the cyclophosphazenes investigated and the properties of the substituents influencing the geometry and the P–N bond system of the ring, semiempirical quantum-chemical calculations have been carried out for model compounds by the CNDO/2 method and the paramagnetic contributions of the shielding constants as well as the interaction constants were calculated.[29–31,35] The calculations were performed in terms of the parametrisation of Pople[60] and Santry;[61] account was taken of the *d* orbitals for phosphorus, whereas only the *s* and *p* orbitals were used for substituents comprising the elements in the Third Period (chlorine and sulphur).

The shielding constant $\sigma_A$ for a nucleus A in the molecule can be represented, according to Ramsay,[62] by the sum of two contributions, which depend on the choice of the origin of coordinates:

$$\sigma_A = \sigma_{dia,A} + \sigma_{para,A} . \qquad (1)$$

The paramagnetic contribution in this equation can be estimated in accordance with the approximation proposed by Pople.[63] The changes in the diamagnetic contributions on passing from one compound to another are small and can therefore be disregarded. According to Pople's approximation mentioned above, the paramagnetic contribution by the given nucleus A can be calculated as follows:

$$\sigma_{para,A} = -\frac{e^2\hbar^2}{2m^2c^2} \cdot \frac{1}{\Delta E} \cdot \langle r_p^{-3} \rangle \cdot \sum_B Q_{AB} , \qquad (2)$$

where

$$Q_{AB} = \frac{4}{3}\delta_{AB}(p_{x_Ax_B} + p_{y_Ay_B} + p_{z_Az_B}) - \frac{2}{3}(p_{y_Ay_B}p_{z_Az_B} + p_{z_Az_B}p_{x_Ax_B} + p_{x_Ax_B}p_{y_Ay_B}) + \frac{2}{3}(p_{y_Az_B}p_{z_Ay_B} + p_{z_Ax_B}p_{z_Bx_A} + p_{x_Ay_B}p_{y_Ax_B}) . \qquad (3)$$

Here B is any atom in the molecule, $\delta_{AB}$ is the Kronecker delta, $p_{ij}$ are the elements of the density matrix, and $\langle r_P^{-3} \rangle$ is the expected value of the reciprocal of the cube of the radius of the 3*p* orbital of phosphorus or the 2*p* orbital of nitrogen. The latter values were calculated from the Hartree–Fock atomic functions[64,65] using a linear interpolation for the non-integral charges.

The 3*d* orbitals of the phosphorus atom are probably also important for the description of the chemical bonds in cyclophosphazene but their influence on the chemical shift is small, because the expected value of the reciprocal of the cube of the radius of the 3*d* orbitals of phosphorus is smaller by several orders of magnitude than the corresponding value for the 3*p* orbitals; the contribution of the 3*d* orbitals is not therefore taken into account in Eqn.(2).

In the calculations of the $^{31}P$ chemical shift in the NMR spectra of cyclophosphazenes, the quantity $\Delta E$ may be regarded as constant and one can thus compare the experimental chemical shifts with the products $\langle r_P^{-3} \rangle \sum_B Q_{AB}$.

It is then found that allowance for the distribution of the charge on the phosphorus atom $\langle r_P^{-3} \rangle Q_{PP}$ alone leads to results which are not in sufficiently good agreement with experimental data. Evidently the bond between phosphorus and the neighbouring nitrogen atoms, taken into account by the quantity $2Q_{PN}$, makes a large contribution to the $^{31}P$ chemical shift, so that comparison of the experimental chemical shifts with the product $\langle r_P^{-3} \rangle (Q_{PP} + 2Q_{PN})$ leads to satisfactory results.[35] Additional allowance for the influence of the atoms of the substituents, expressed in terms of $2Q_{PX}$, does not entail an appreciable improvement of the agreement between the calculation and experiment.

Quantum-chemical calculations have been performed for the following compounds: $(NPF_2)_3$, $(NPF_2)_4$, $(NPCl_2)_3$, $(NPCl_2)_4$, and $[NP(CH_3)_2]_3$. $[NP(OH)_2]_3$, $[NP(OH_2]_4$, $[NP(SH)_2]_3$, $[NP(NH_2)_2]_3$, and $[NP(NH_2)_2]_4$ were chosen as model compounds for the ethers, thioethers, and amino-derivatives.[30,31] The planar molecular structure was adopted for cyclotriphosphazenes and the tetrameric fluoro-derivative, while the structures of other cyclotetraphosphazenes were assumed to be in the form of a saddle with approximately $D_{2d}$ symmetry.[29] The bond lengths and bond angles were taken from the literature (for example, Allcock[56]) or were estimated for model compounds.

Fig.2 illustrates the correlation between the chemical shift $\delta$P and the quantity

$$\langle r_p^{-3}\rangle \sum_B Q_{AB}$$

for cyclotriphosphazene. With an increase of the positive charge on the phosphorus atom, the paramagnetic component as a rule diminishes, which is evident from the comparison of data for substituents in the series C, N, O, F and also Cl, F and S, O. However, when the substituents C and Cl are compared, an increase of the paramagnetic contribution is observed. The coefficient of the correlation between the chemical shift and the calculated paramagnetic contribution, amounting to 0.74, is not satisfactory. The points for the chloro-derivative and the thioether in Fig.2 deviate markedly from the regression line. If account is taken only of compounds in which the substituent atoms are those of elements in the Second Period in Mendeleev's table, a better correlation coefficient is obtained (0.88). This is also observed for the correlations with other NMR parameters (see below). The deviations observed for substituent atoms which are those of elements in the Third Period, arise owing to the lack of validity of the method of approximation employed. Fig.2 does not include compounds containing a phenyl group (the anilino-, phenoxy-, and phenylthio-derivatives), since the phenyl group has a strong influence on the $^{31}$P chemical shift.

An analogous correlation has been observed for cyclotetraphosphazenes between the $^{31}$P chemical shift and the quantity

$$\langle r_p^{-3}\rangle \sum_B Q_{AB}.$$

The change in $\delta$P in the upfield direction with increase of ring size and specially the marked change in $\delta$P on passing from cyclotriphosphazene to cyclotetraphosphazene cannot be explained by the distribution of electrons at the phosphorus atom alone, because it is virtually the same for the trimers and tetramers; in these cases too it is essential to take into account the contributions of the bonds with the neighbouring nitrogen atoms. The cause of the change in the chemical shift should be sought primarily in the change of the contribution of the bonding $3p-2p$ orbitals on passing from the planar trimeric compounds to the nonplanar tetrameric compounds.[35] In the case of the fluoroderivative the large change in $\delta$P on passing from cyclotriphosphazenes to cyclotetraphosphazenes must have other causes, because the planar structure is retained in this instance.[29] Indeed it is found that the change in $\delta$P is not adequately described by the values of

$$\langle r_p^{-3}\rangle \sum_B Q_{AB},$$

if it is assumed that

$$\sum_B Q_{AB} = Q_{PP} + 2Q_{PN}.$$

This change in $\delta$P can be described more adequately if account is taken of transannular bonds with other phosphorus atoms ($2Q_{P\ldots P}$). These transannular bonds are particularly marked in hexafluorocyclotriphosphazene.[35]

Numerous studies have been devoted to cyclophosphazenes with mixed substituents. Data on the $^{31}$P chemical shifts are presented in monographs[56,67-70] and numerous later publications. Cyclotriphosphazenes with mixed substituents, giving rise to spectra of the $A_2X$, $A_2B$, AMX, ABX, or ABC

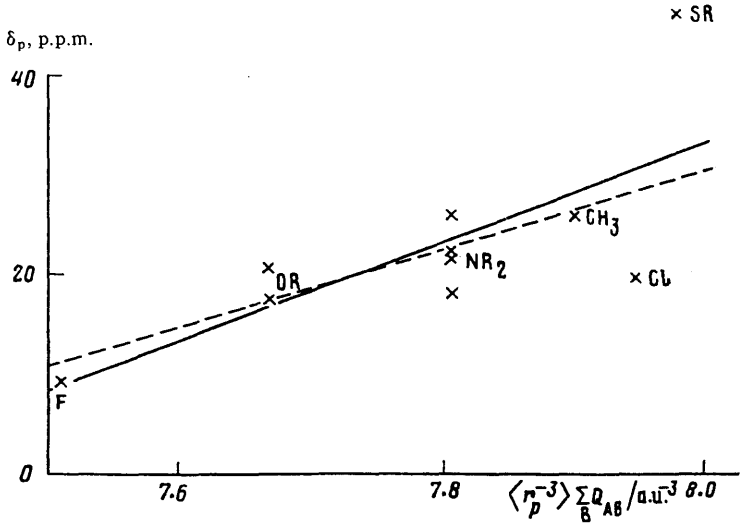



Figure 2. Correlation between the $^{31}$P chemical shift in the NMR spectra of compounds of the type $(^{15}NPR_2)_3$ and the quantity $\langle r_p^{-3}\rangle \sum_B Q_{AB}$; the correlation coefficients are $r = 0.74$ (continuous line) and $r = 0.88$ (dashed line); the crosses represent experimental points.

types, as well as a series of cyclotetraphosphazenes with mixed substituents for which there is a possibility of spectra of types $A_2X_2$, $A_2B_2$, AA'XX', $A_2MX$, $A_2BX$, $A_2BC$, ABMX, ABXY, ABCX, ABCD, and AA'BB', were investigated in the first place. Since higher-order spectra are observed in many cases, the exact chemical shifts and interaction constants can be obtained only by modelling the spectra.

The available $^{31}P$ chemical shifts provide answers to the questions how the chemical shift changes when two different substituents are attached to the same phosphorus atom and what is the influence of the substituents at the other phosphorus atoms. Answers to these questions have been provided in relation to the series $N_3P_3Cl_{6-n}(SEt)_n$ ($n = 0-6$) and $N_4P_4Cl_{8-n}(SEt)_n$ ($n = 0-8$), in which geminally substituted compounds are formed exclusively.[51] In the selected examples the chemical shifts for the phosphorus atoms with two identical substituents, i.e. for $PX_2$ and $PY_2$, differ markedly and the chemical shifts for phosphorus atoms with mixed substituents (PXY) are always intermediate between these values (but are not their averages). In the case of aminochlorophosphazenes, where the shifts change only slightly on passing from $PX_2$ to $PY_2$ (Table 1), the $\delta$P for PXY are sometimes not intermediate between these values.[13,22] Thus the fact, known for other phosphorus compounds, that the dependence of the chemical shift of phosphorus on the contributions of the substituents is not additive, has been confirmed also for cyclophosphazenes. For this reason attempts are no longer made to create a system of increments for the empirical calculation of the chemical shifts similar to the systems which exist for $^{1}H$ and $^{13}C$. The finding[72] that the chemical shift for phosphorus atoms with mixed substituents is usually displaced downfield compared with the average value holds also for cyclophosphazenes (Tables 2 and 3).

**Table 1.** $^{31}P$ Chemical shifts (in p.p.m.*) for cyclophosphazenes of the type $(NPR_2)_n$.

| Compound | $n=3$ | $n=4$ | $n=5$ | $n=6$ |
|---|---|---|---|---|
| $(NPMe_2)_n$ | 26.1 | 19.9 | 14.9 | — |
| $[NP(NH_2)_2]_n$ | 15.9** | — | — | — |
| $[NP(NHMe)_2]_n$ | 22.3 | 10.2 | — | — |
| $[NP(NHEt)_2]_n$ | 18.1 | 6.4 | — | — |
| $[NP(NHPh)_2]_n$ | 4.9*** | — | — | — |
| $[NP(NMe_2)_2]_n$ | 26.0 | 10.2 | 3.1**** | 0.5**** |
| $[NP(NEt_2)_2]_n$ | 21.9 | 6.2 | — | — |
| $[NP(OMe)_2]_n$ | 20.8 | 2.4 | −2.0 | −4.3 |
| $[NP(OEt)_2]_n$ | 17.6 | 0.8 | — | — |
| $[NP(OPh)_2]_n$ | 8.7 | −12.4 | — | — |
| $[NP(SEt)_2]_n$ | 46.3 | 25.1 | — | — |
| $[NP(SPh)_2]_n$ | 43.4 | — | — | — |
| $(NPF_2)_n$ | 9.3 | −17.7 | −21.9 | — |
| $(NPCl_2)_n$ | 20.0 | −6.5 | −15.5 | −17.5 |
| $(NPBr_2)_n$ | −44.2 | −69.9 | −78.1 | — |

*Standard—85% phosphoric acid; positive values denote a downfield shift.

**In aqueous solution.

***Saturated solution in $CDCl_3$.

****The value of $\delta$p depends strongly on the solvent.

The effect of substituents at other phosphorus atoms on the $\delta$p is also evident from the data presented in Tables 2 and 3. The change in $\delta$p is by several p.p.m. for the identical immediate environment of the phosphorus atom and a distinct regularity is not observed. It is known that the bond lengths and angles in cyclophosphazenes vary quite markedly when substituents are introduced. The change in the geometry of the environment of the phosphorus atom can be to some extent responsible for the change in $\delta$p.

Table 2. $^{31}P$ Chemical shifts (in p.p.m.) for chloro(ethylthio)cyclotriphosphazenes.

| Compound | Structural groups at P atoms | | |
|---|---|---|---|
| | $\equiv PCl_2$ | $\equiv PClSEt$ | $\equiv P(SEt)_2$ |
| $N_3P_3Cl_5$ | 20.0 | — | — |
| $N_3P_3Cl_5SEt$ | 21.0 | 33.1 | — |
| $N_3P_3Cl_4(SEt)_2$ | 18.7 | — | 51.3 |
| $N_3P_3Cl_3(SEt)_3$ | 18.1 | 38.5 | 50.6 |
| $N_3P_3Cl_2(SEt)_4$ | 17.4 | — | 49.2 |
| $N_3P_3Cl(SEt)_5$ | — | 37.1 | 48.0 |
| $N_3P_3(SEt)_6$ | — | — | 46.5 |
| Mean value | 19.0 | 36.2 | 49.1 |

Table 3. $^{31}P$ Chemical shift (in p.p.m.) for chloro(ethylthio)cyclotetraphosphazenes.

| Compound | Structural groups at P atoms | | |
|---|---|---|---|
| | $\equiv PCl_2$ | $\equiv PClSEt$ | $\equiv P(SEt)_2$ |
| $N_4P_4Cl_8$ | −6.5 | — | — |
| $N_4P_4Cl_6(SEt)_2$ | −7.1; −8.2 | — | 30.4 |
| 2,2,4-$N_4P_4Cl_5(SEt)_3$ | −8.0; −8.9 | 13.5 | 29.7 |
| 2,2,6-$N_4P_4Cl_5(SEt)_3$ | −8.2 | 14.6 | 29.4 |
| 2,2,4,4-$N_4P_4Cl_4(SEt)_4$ | −8.7 | — | 27.9 |
| 2,2,6,6-$N_4P_4Cl_4(SEt)_4$ | −8.8 | — | 29.4 |
| 2,2,4,4,6-$N_4P_4Cl_3(SEt)_5$ | −9.4 | 12.7 | 26.9 |
| 2,2,4,6,6-$N_4P_4Cl_3(SEt)_5$ | −9.5 | 12.2 | 28.1 |
| $N_4P_4Cl_2(SEt)_6$ | −9.5 | — | 26.9; 26.0 |
| $N_4P_4(SEt)_8$ | — | — | 25.1 |
| Mean value | −8.4 | 13.3 | 28.0 |

An attempt has been made recently[74] to calculate the $^{31}P$ chemical shifts for a series of geminally disubstituted tetrachlorocyclotriphosphazenes from the increments in the shifts caused by substituents. Very satisfactory results have been obtained for the dialkyl derivatives probably because the changes in the chemical shifts in this group of compounds are small. In the case of compounds with mixed alkyl and halogeno-substituents, appreciable deviations are observed unless special corrections are applied. For *para*-substituted monoarylphosphazenes, Harris[74] observed a satisfactory correlation with the Hammet $\sigma$ parameters.

## III. $^{15}N$ CHEMICAL SHIFTS

Chemical shift data for endocyclic nitrogen atoms were published by ourselves for $^{15}N$-labelled cyclophosphazenes.[20-23,28,30,35,55] Apart from these data, the results of Mason and co-workers,[19] who used the broad line $^{14}N$ NMR, are available in the literature. These results are not accurate, since they were obtained under different conditions (without a solvent, in the melt, and in various solvents) and, furthermore, the line width is in the range 165–700 Hz. A detailed analysis of the experimental chemical shifts of nitrogen is possible only when $^{15}N$ NMR is used.

Table 4 presents the nitrogen chemical shifts for cyclophosphazenes with identical substituents, which we obtained in the study of endocyclic $^{15}N$-labelled compounds. The

measurements were performed for solutions of the compound in $CDCl_3$; the exceptions will be indicated separately.

Mason et al.[19] obtained the following series based on the influence of the substituents at the phosphorus atom on the nitrogen chemical shift:

$$NMe_2 > OMe > F > NCS > Cl > Br .$$

This sequence does not coincide either with that observed for the $^{31}P$ shift or with the reverse of the latter. The authors[19] attempted to give a semiempirical explanation of the phosphorus and nitrogen chemical shifts; they were able to establish a correlation by comparing the paramagnetic contributions of the atom–ligand system for phosphorus and nitrogen, i.e. the contributions which include the diamagnetic component of the ligand.[75]

**Table 4.** $^{15}N$ Chemical shifts (in p.p.m. relative to nitromethane) for cyclophosphazenes with substituents of one kind and different ring sizes.

| Compound | n=3 | n=4 | n=5 | n=6 |
|---|---|---|---|---|
| $(^{15}NPMe_2)_n$ | −319.5 | −300.0 | — | — |
| $(^{15}NP(NH_2)_2)_n$ | −298.3* | — | — | — |
| $(^{15}NP(NHMe)_2)_n$ | −315.1 | — | — | — |
| $(^{15}NP(NHEt)_2)_n$ | −312.4 | −306.7 | — | — |
| $(^{15}NP(NMe_2)_2)_n$ | −320.8 | −314.8 | −317.0 | −317.6 |
| $(^{15}NP(NEt_2)_2)_n$ | −316.3 | — | — | — |
| $(^{15}NP(OMe)_2)_n$ | −317.8 | −313.7 | −318.9 | −320.0 |
| $(^{15}NP(OEt)_2)_n$ | −314.3 | — | — | — |
| $(^{15}NP(OPh)_2)_n$ | −305.9 | −302.5 | — | — |
| $(^{15}NP(SEl)_2)_n$ | −284.2 | −270 | — | — |
| $(^{15}NP(SPh)_2)_n$ | −285.0 | — | — | — |
| $(^{15}NPF_2)_n$ | −314.5 | −314.4 | −322.8 | — |
| $(^{15}NPCl_2)_n$ | −258.8 | −248.0 | −253.1 | −253.3 |
| $(^{15}NPBr_2)_n$ | −240.1 | −230.8 | — | — |

*Solution in water; in the remaining cases—solution in $CDCl_3$.

The virtual absence of a difference in the $\delta_N$ for different substituent atoms of elements in the Second Period attached to the phosphorus atom is striking in the study of the nitrogen chemical shift. For example, on passing from alkylphosphazene to the fluoro-derivative in the series of cyclotriphosphazenes, the chemical shift $\delta_N$ changes by only 5 p.p.m. This finding is particularly surprising in view of the fact that the basicities of the above phosphazenes differ markedly[76] and the basicity centres are in fact located at the ring nitrogen atoms. Evidently there is no direct relation between the basicity and the nitrogen chemical shift.

The $^{15}N$ chemical shift varies markedly for phosphazenes with substituents involving elements belonging to the same Group. For example, on passing from fluoro- to bromocyclotriphosphazene, the chemical shift increases by 74.4 p.p.m., while in the case of the corresponding cyclotetraphosphazenes the increase is by 83.6 p.p.m. In order to account for these changes, one cannot assume that $\Delta E$ is constant in the series of similar compounds, because the nodal planes of the $\pi$ orbitals or the non-bonding $p$ orbitals pass through the $^{15}N$ nucleus or in its vicinity.[35] Such orbitals exert a major influence on the shielding of the nucleus.[77] As in the interpretation of the $^{17}O$ chemical shifts by one of the present authors and his co-workers,[78] the difference between the energies of the lowest unoccupied and the highest occupied orbitals, where the $\pi$ electrons of nitrogen are mainly localised, was adopted as a measure of $\Delta E$:

$$\Delta E = \epsilon_{LUMO} - \epsilon_{HOMO} .$$

The relation between $\delta_N$ and $\Delta E$ is illustrated in Fig. 3. The slight change in $\delta_N$ in the presence of substituents comprising elements of the Second Period corresponds to a slight change in $\Delta E$ and a marked change in $\delta_N$ within the Groups and also corresponds to a marked change in $\Delta E$.

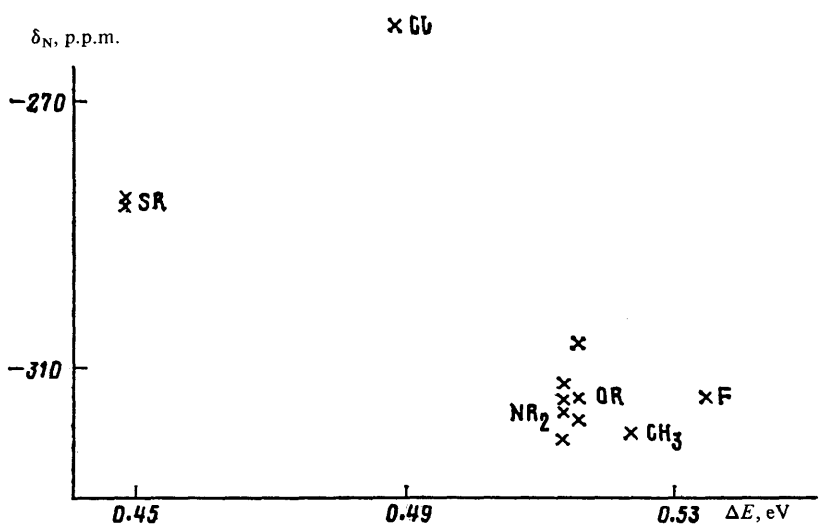



**Figure 3.** Dependence of the $^{15}N$ chemical shift on the calculated value of $\Delta E$ for cyclophosphazenes of the type $(^{15}NPR_2)_3$.

However, the $\Delta E$ for the thioethers is smaller than would be expected from the upfield displacement of $\delta_N$ relative to the chloro-derivative. This deviation can be caused by the fairly considerable contribution of the sulphur orbitals to the HOMO.

The $^{15}N$ chemical shift in the NMR spectra of cyclotetraphosphazenes has undergone a downfield displacement compared with the spectrum of cyclotriphosphazenes. This is probably caused by the change in molecular structure to a non-planar form, indicated by the identical chemical shifts for the compounds $(^{15}NPF_2)_3$ and $(^{15}NPF_2)_4$. The $^{15}N$ chemical shift for the pentameric cyclophosphazenes has undergone an upfield displacement compared with the spectrum of the tetrameric cyclophosphazenes, which can be accounted for by the fact that, on passing from $(NPR_2)_4$ to $(NPR_2)_5$, the quantity $\Delta E$ should change only slightly, while $Q_{PN}$ should diminish, which agrees with the change in the $^{31}P$ chemical shift. In the calculation of the paramagnetic contribution in the case of $^{15}N$ account is also taken of the values of $Q_{PN}$, as for $^{31}P$, and the above analogy in the instances quoted is understandable. On further increase of ring size, $\delta_N$ undergoes a slight upfield shift and probably approaches a limiting value.[55]

Cyclophosphazenes with mixed substituents but with identical substituents at the phosphorus atoms adjoining the nitrogen atom are characterised by a $^{15}N$ chemical shift which is almost independent of the substituents at the phosphorus atom remote from the ring nitrogen atom. In this case a simpler picture is observed than for the $^{31}P$ NMR spectra. The shifts $\delta_N$ for the phenylamino-derivatives of cyclotriphosphazene and cyclotetraphosphazene are presented as an example in Tables 5 and 6.

**Table 5.** $^{15}N$ Chemical shifts (in p.p.m.) for chloro(phenylamino)cyclotriphosphazenes.

| Compound | $PCl_2$–N–$PCl_2$ | $PCl_2$–N–PClNHPh | $PCl_2$–N–P(NHPh)$_2$ |
|---|---|---|---|
| $^{15}N_3P_3Cl_6$ | −258.8 | — | — |
| $^{15}N_3P_3Cl_5NHPh$ | −256.3 | −268.1 | — |
| $^{15}N_3P_3Cl_4(NHPh)_2^*$ | −255.1 | — | −279.1 |
| Mean value | −256.7 | — | — |

*Geminal substitution.

**Table 6.** $^{15}N$ Chemical shifts (in p.p.m.) for chloro(phenylamino)cyclotetraphosphazenes.[23]

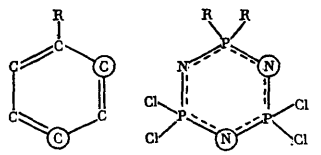
| Compound | $PCl_2$–N–$PCl_2$ | $PCl_2$–N–PClNHPh | PClNHPh–N–PClNHPh |
|---|---|---|---|
| $^{15}N_4P_4Cl_8$ | −248.0 | — | — |
| $^{15}N_4P_4Cl_7NHPh$ | −246.7 | −260.1 | — |
| 6,8-$^{15}N_4P_4Cl_6(NHPh)_2$ | −244.5 | −259.2 | −275.5 |
| 4,8-$^{15}N_4P_4Cl_6(NHPh)_2$ | — | −259.2* | — |
| Mean value | −246.4 | −259.5 | — |

*Solution in $(CD_3)_2CO$.

The values of $\delta_N$ for the same ring size depends mainly on the nature of the substituents at the neighbouring phosphorus atoms. A fairly linear relation between $\delta_N$ and the degree of substitution is observed regardless of whether the substitution is geminal or non-geminal. It is easily seen that the shifts quoted in the middle columns of Tables 5 and 6 are approximately equal to the arithmetical means of the values in the extreme columns. The same type of behaviour has been observed also for linear phosphazenes; for example, in the series of compounds $(EtO)_nCl_{3-n}P = N-P(O)(OEt)_mCl_{2-m}$, where $n = 0-3$ and $m = 0$ or $n = 3$ and $m = 1$ or 2, the gradual substitution of chlorine by ether groups entails a uniform upfield displacement of $\delta_N$.[79] The additivity of the influence of substituents on the chemical shift of nitrogen holds also for all other cyclophosphazenes which we investigated: $^{15}N_3P_3Cl_4F_2$,[21] $^{15}N_3P_3Cl_4(SEt)_2$,[20,21] $^{15}N_3P_3Cl_4(SPh)_2$ and $^{15}N_3P_3Cl_2(SPh)_4$,[20] and $^{15}N_4P_4Cl_4(SEt)_4$[20] and $^{15}N_3P_3Cl_4.(NH_2)_2$.[21]

The effect of substituents at phosphorus atoms which do not adjoin the given nitrogen atom on $\delta_N$ is insignificant in all the cases investigated. The electronic structure of cyclophosphazenes differs clearly from the delocalised aromatic bond system in cyclic organic compounds (Table 7). An appreciable influence of substituents on the $^{13}C$ NMR chemical shift has been observed in many instances in the case of monosubstituted benzenes for atoms in both *ortho*- and *para*-positions (transmission of the influence of substituents via the delocalised system of ring $\pi$ electrons), while for the geminally disubstituted cyclotriphosphazenes a marked influence only the neighbouring nitrogen atom is observed. The absence of an appreciable long-range influence is evidence against the ring delocalisation of $\pi$ electrons in cyclophosphazenes (see also, Thomas et al[22]).

**Table 7.** $^{13}C$ Chemical shifts for monosubstituted benzenes[80] and the $^{15}N$ chemical shifts for geminally disubstituted cyclotriphosphazenes.[21]



| R | $\delta_C$ | $\Delta\delta_C$ | $\delta_N$ | $\Delta\delta_N$ | $\Delta\delta_{N/n\,R}$ |
|---|---|---|---|---|---|
| | | | *o*-Position | | |
| Cl | 128.9 | 0 | −258.0 | 0 | 0 |
| F | 115.1 | −13.8 | −286.9 | −28.1 | −14.05 |
| $NH_2$ | 115.5 | −13.4 | −272.8 | −14.1 | −7.05 |
| SEt | 129.2 | 0.3 | −270.0 | −12.1 | −6.05 |
| | | | *p*-Position | | |
| Cl | 126.6 | 0 | −258.8 | 0 | 0 |
| F | 124.1 | −2.5 | −259.8 | −1.0 | −0.5 |
| $NH_2$ | 118.5 | −8.1 | −255.5 | 3.3 | 1.65 |
| SEt | 125.9 | −0.7 | −255.9 | 2.9 | 1.45 |

## IV. $^{31}P-^{15}N$ SPIN–SPIN COUPLING CONSTANTS

The spin–spin coupling constants $^1J_{PN}$ have been determined in recent years for individual compounds and also for a series of different classes of compounds (mainly for organophosphorus compounds), using both $^{15}N$-enriched materials and compounds with the natural abundance of isotopes.[81-90] We determined the $^1J_{PN}$ coupling constants for $^{15}N$-labelled cyclophosphazenes.[20-23,27,28,30,35,55] The interaction constants for different cyclophosphazenes with substituents of one kind are compared in Table 8.

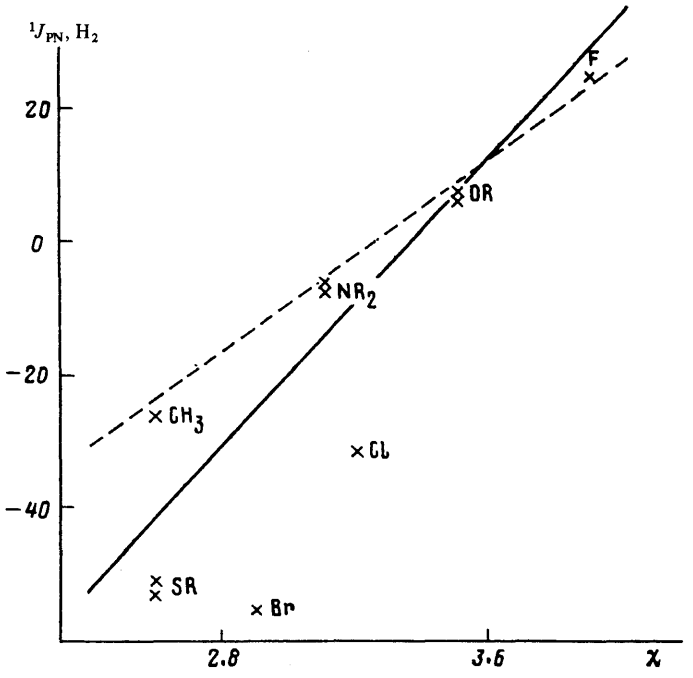



**Figure 4.** Correlation between the coupling constant $^1J_{PN}$ for compounds of the type $(^{15}NPR_2)_3$ and the electronegativity of the substituent atoms χ; the correlation coefficients are $r = 0.83$ (continuous line) and $r = 0.99$ (dashed line).

**Table 8.** Coupling constants $^1J_{PN}$ (in Hz) for cyclophosphazenes with substituents of one kind and different ring sizes.*

| Compound | n=3 | n=4 | n=5 | n=6 |
|---|---|---|---|---|
| $(^{15}NPMe_2)_n$ | −26.1 | −23.8 | — | — |
| $[^{15}NP(NH_2)_2]_n$ | 1.6** | — | — | — |
| $[^{15}NP(NHMe)_2]_n$ | −7.7 | — | — | — |
| $[^{15}NP(NHEt)_2]_n$ | −7.8 | 5.5 | — | — |
| $[^{15}NP(NHPh)_2]_n$ | −6.6 | — | — | — |
| $[^{15}NP(NMe_2)_2]_n$ | −7.5 | 14.2 | 19.4 | 29.3 |
| $[^{15}NP(NEt_2)_2]_n$ | −6.1 | — | — | — |
| $[^{15}NP(OMe)_2]_n$ | 7.5 | 32.7 | 39.0 | 41.5 |
| $[^{15}NP(OEt)_2]_n$ | 6.4 | — | — | — |
| $[^{15}NP(OPh)_2]_n$ | 7.1 | 37.5 | — | — |
| $[^{15}NP(SEt)_2]_n$ | −51.0 | −34.0 | — | — |
| $[^{15}NP(SPh)_2]_n$ | −53.3 | — | — | — |
| $(^{15}NPF_2)_n$ | 24.9 | 68.8 | 71.8 | — |
| $(^{15}NPCl_2)_n$ | −31.7 | −6.9 | −3.0 | −2.0 |
| $(^{15}NPBr_2)_n$ | −55.8 | −35.5 | — | — |

*The signs of the constants were not determined experimentally.

**For such a low value of the constant, it is impossible to predict the sign of the latter.

It was found that the absolute values of the coupling constant $^1J_{PN}$ are not correlated either with the parameters of the P–N bond or with those of the substituent. In order to account for the observed changes in $^1J_{PN}$ as a

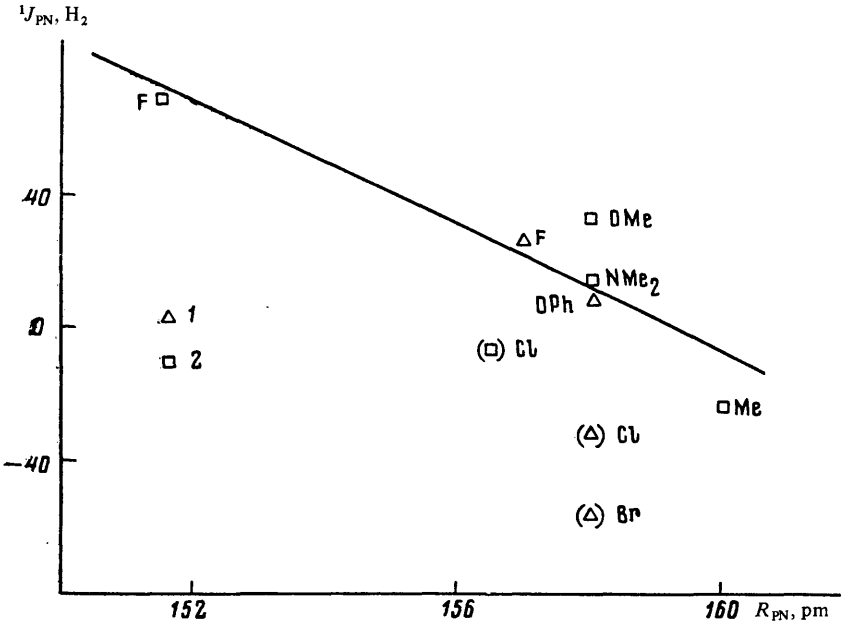



**Figure 5.** Correlation between $^1J_{PN}$ and the PN bond length ($R_{PN}$) for cyclotriphosphazenes (1) and cyclotetraphosphazenes (2). The continuous line corresponds to the correlation coefficient $r = 0.91$.

function of the position in the Mendeleev table of substituents linked directly to the phosphorus atom considered, it was necessary to assume that the increase of the atomic number of the substituent element within a Period and within a Group entails the reversal of the sign of $^1J_{PN}$. It is known from the literature[90-92] that $^1J_{PN}$ can be both positive and negative. The sign changes probably within the framework of one class of compounds. Since in most cases it was impossible to determine experimentally the sign of the coupling constants for cyclophosphazenes, the signs were selected in such a way that the changes in $^1J_{PN}$ were reasonable (Table 8). The legitimacy of this approach is confirmed by the results obtained for geminally disubstituted cyclotriphosphazenes[21] and for endocyclically $^{15}N$-labelled chloro(phenylamino)cyclotetraphosphazenes[23] (see below).

The coupling constants thus obtained are satisfactorily correlated with the electronegativity of the substituents atoms linked directly to the phosphorus atom, which can be seen in relation to cyclotriphosphazenes (Fig.4). The correlation coefficient is 0.83; an improved correlation ($r$ = 0.991) can be achieved by considering only the elements of the Second Period as the substituents. The same relations are observed in the series of cyclotetraphosphazenes.[28] The correlation established between the coupling constants $^1J_{PN}$ and the electronegativity of the substituent atoms is as expected, since the structure of the P–N bond systems in cyclophosphazenes depends to a large extent on the nature of the substituents.

In addition, Table 8 shows that $^1J_{PN}$ increases with increasing ring size when cyclophosphazenes with substituents of only one kind are considered and in most cases the greatest change is observed on passing from trimeric to tetrameric phosphazenes.

The examples presented below show that there is a linear correlation between the P–N coupling constant and other experimental data for the molecules. When the $^1J_{PN}$ and the P–N bond lengths for cyclotriphosphazenes and cyclotetraphosphazenes are compared (Fig.5), it is again striking that a satisfactory correlation is observed when account is taken only of the substituents whose atoms, linked to the phosphorus atom, are those of elements in the Second Period. The scatter of the points around the regression line can be accounted for to some extent as, on the one hand, the bond lengths are specified only to within 0.5 pm or even 1 pm (in the main the literature data were taken from the 1960s) and, on the other hand, the bond lengths can change somewhat on passing from a solid to a solution.

The constants $^1J_{PN}$ for cyclophosphazenes are in the given instance extremely sensitive to changes in the P–N bond lengths: when $d_{PN}$ changes from 151 pm in $N_4P_4F_8$ to 160 pm in $N_4P_4Me_8$, the P–N coupling constant changes from +68.8 Hz to -23.8 Hz. Compared with this, the change in the coupling constant $^1J_{CC}$ resulting from the marked alteration of the C–C bond length on passing from ethane (153 pm) to ethylene (134 pm) and acetylene (121 pm) is relatively small—from 34.6 Hz[94] to 67.6 Hz[95] and 171.5 Hz.[95]

Comparison of the P–N interaction constants with the frequencies of the antisymmetric stretching vibrations obtained from the infrared spectra reveals a very satisfactory correlation for substituents in which an element of the Second Period is linked to phosphorus (Fig.6). For other substituents, an appreciable deviation from this relation is observed; however, Fig.6 shows that some regularities can be observed for these elements too (this is indicated by dashed lines connecting points for substituent elements of the Third Period and the halogens).

It has been observed for pyridine and the pyridinium ion[93] that the free electron pair localised at the nitrogen atom influences the interaction constant $^1J_{NC}$. Since the free electron pair localised at the nitrogen atom in cyclophosphazenes is responsible for their basic properties, there should have been a direct relation between $^1J_{PN}$ and the basicities of the corresponding compounds. In fact such a relation is observed only within the limits of a single Period. An increase in the basicity of cyclophosphazenes[76] corresponds to a decrease of the P–N interaction constant.

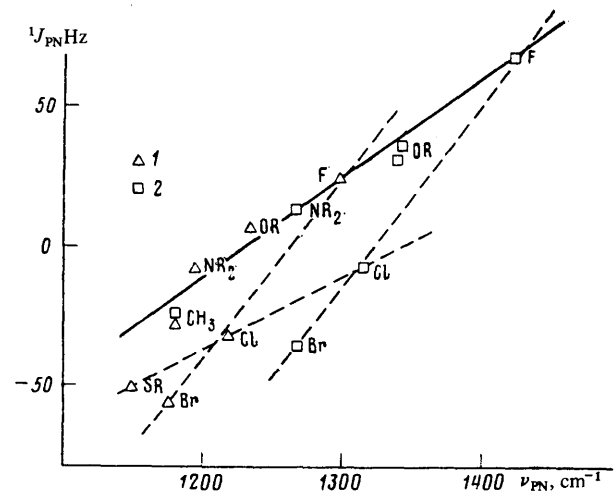



Figure 6. Correlation between $^1J_{PN}$ and the antisymmetric stretching vibration frequency for cyclotriphosphazenes (1) and cyclotetraphosphazenes (2); the correlation coefficient $r$ = 0.87 in all cases.

For a qualitative interpretation of the coupling constants, quantum-chemical model calculations were performed by the CNDO/2 method. The indirect spin–spin coupling constant is determined by three contributions: the Fermi contact contribution (*FC*), the orbital contributions (*OD*), and the spin–dipole contribution (*SD*). For coupling via one bond, the last two contributions are much smaller than that of the Fermi contact interaction and it is therefore possible to consider only the latter. Our calculations did indeed show that the *FC* contribution is greater by two orders of magnitude than the others, which is also confirmed by the data of a number of other investigators. For example, a linear correlation has been observed[83,84] between the experimental coupling constants and the *FC* contributions, also calculated by the CNDO/2 method using the theory of finite perturbations. On the other hand, Duangthai and Webb,[96] who used the INDO method, found, that, although the *SD* contribution remains small, nevertheless the orbital *OD* contribution plays an appreciable role, particularly when it is necessary to obtain the absolute values of the coupling constant.

According to Pople, the expression for the *FC* contribution in terms of the $\Delta E$ approximation is

$$J_{AB}^{FC} = \frac{32}{9}\pi\hbar\gamma_A\gamma_B\beta^2\,(^3\Delta E)^{-1}\langle s_A|\delta(r_A)|s_A\rangle\langle s_B|\delta(r_B)|s_B\rangle\, p^2_{s_As_B}\,, \quad (4)$$

where $\gamma_A$ and $\gamma_B$ are the gyromagnetic ratios of the interacting nuclei, $\beta$ is the Bohr magneton, $^3\Delta E$ the "average triplet excitation energy", $\langle s|\delta(r)|s\rangle$ the expected value

of the 2s or 3s function at the location of the nucleus, and $p_{s_A s_B}$ the order of the s-bond. Assuming that

$$K_{AB} = \frac{2\pi}{\hbar\gamma_A\gamma_B} J_{AB} , \quad (5)$$

it is possible to obtain the conventional coupling constant $K_{AB}$:

$$K_{AB}^{FC} = \frac{64}{9}\pi^2\beta^2 (^3\Delta E)^{-1} \langle s_A|\delta(r_A)|s_A\rangle\langle s_B|\delta(r_B)|s_B\rangle p^2_{s_A s_B} . \quad (6)$$

If it is assumed that $\Delta E$ and the expected values of the s-function do not vary, then the interpretation of the experimental coupling constants reduces to their comparison with the square of the s-bond order.

Examination of the experimental coupling constant $^1J_{PN}$ as a function of the calculated *FC* contribution jointly for cyclotriphosphazenes and cyclotetraphosphazenes yields the relation in the form of a regression line (Fig.7). For compounds with substituent elements of the Second Period, a very satisfactory correlation coefficient, amounting to 0.990, has been obtained. The inclusion in the consideration of compounds with substituent elements of the Third Period results in an appreciable worsening of the correlation.

Our method of calculation does not allow the observation of a change in the sign of the coupling constant. The quantum-chemical methods of calculation used in other studies[83,96] lead to different signs of $^1J_{PN}$. However, the changes in the signs of the coupling constants observed in these investigations[83,96] are due to the appreciable differences between the structures of the compounds considered. It has been found[90] that $^1J_{PN}$ depends greatly on the coordination number and hence on the bond system of the phosphorus atom involved in the coupling. These observations were subsequently confirmed. In a later study[96] devoted to the interpretation of the coupling constants $^1J_{PN}$ known at the time, certain refinements were introduced: the constant for coupling with tricoordinate phosphorus was found to be positive, electronegative substituents at the interacting P or N atoms increasing the s-electron density at the nuclei and hence increasing the coupling constant. For tetracoordinate phosphorus, negative coupling constants are frequently observed. Here the decisive factor, determining the sign of the constants, becomes the s character of the free electron pair at the nitrogen atom.

In cyclophosphazenes with identical ring sizes, a marked variation of the geometry is not observed when the nature of the substituent is altered; an exception is the fluorotetramer, having, in contrast to other cyclotetraphosphazenes, a planar ring structure. The marked change in the coupling constant on passing from $(^{15}NPF_2)_3$, for which $J_{PN}$ = +24.9 Hz, to $(^{15}NPBr_2)_3$ with $J_{PN}$ = −55.8 Hz must be caused by the different electron negativities of the substituents at the phosphorus atoms (Fig.4).

Table 9. Coupling constants $^1J_{PN}$ (in Hz)* for compounds of the type $^{15}N_3P_3Cl_{6-n}(SPh)_n$ (where $n$ = 0, 2, 4, or 6).

| Compound | Type of P–N bond** | | | |
|---|---|---|---|---|
| | I | II | III | IV |
| $N_3P_3Cl_6$ | −31.7 | — | — | — |
| $N_3P_3Cl_4(SPh)_2$ | −33.7 | −39.4 | −50.6 | — |
| $N_3P_3Cl_2(SPh)_4$ | — | −39.7 | −50.9 | −53.5 |
| $N_3P_3(SPh)_6$ | — | — | — | −53.3 |
| Mean value | −32.7 | −39.55 | −50.75 | −53.4 |

*The sign of the constants were not determined experimentally.

**The P–N bond types I, II, III, and IV correspond to isolated P–N bonds in the fragments $Cl_3P{-}N{-}PCl_2$, $Cl_2P{-}NP(SPh)_2$, $Cl_2PN{-}P(SPh)_2$, and $(PhS)_2P{-}N{-}P(SPh)_2$ respectively.

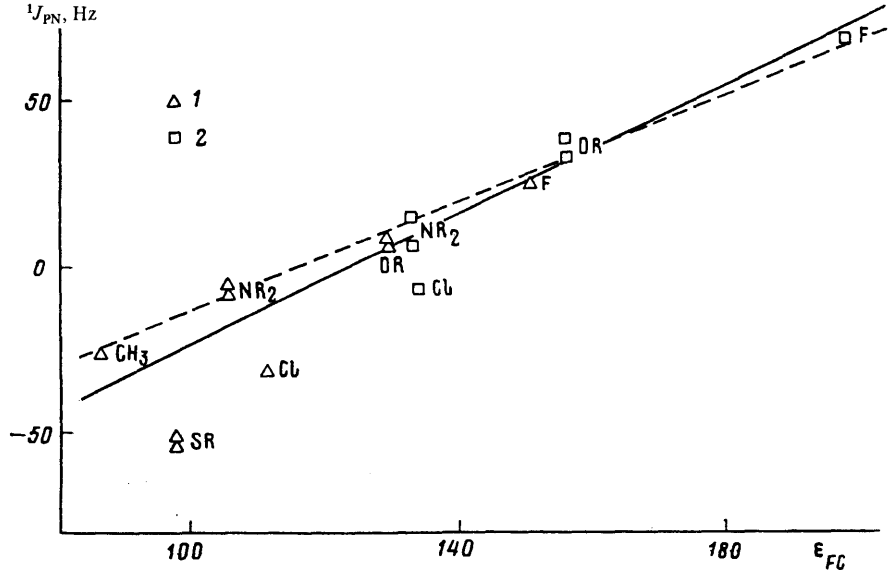



**Figure 7.** Correlation between $^1J_{PN}$ and the contribution of the Fermi contact interaction $\varepsilon_{FC}$ for cyclotriphosphazenes (1) and cyclotetraphosphazenes (2); the correlation coefficients are $r$ = 0.90 (continuous line) and $r$ = 0.990 (dashed line).

Tables 9 and 10 illustrate the influence of the nature of the substituents on the coupling constants $^1J_{PN}$ in relation to chloro(phenylthio)cyclotriphosphazenes[20] and chloro(phenylamino)cyclotetraphosphazenes.[16] The values of $^1J_{PN}$ depend in the first place on the nature of the substituents at the phosphorus atom involved in the P–N coupling considered and only then on the substituents at the other phosphorus atom linked to the given nitrogen atom. It is seen from Tables 9 and 10 that the differences between the coupling constants for bonds of types II and III are much greater than between the constants for bonds of types I and II or III and IV, the differences between the constants for bonds of one type being insignificant.

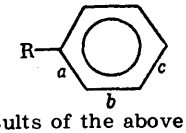
**Table 10.** Coupling constants $^1J_{PN}$ (in Hz) for chloro(phenylamino)cyclotetraphosphazenes $^{15}$N-labelled endocyclically.

| Compound | Type of P–N bond* | | | |
|---|---|---|---|---|
| | I | II | III | IV |
| $N_4P_4Cl_8$ | −6.9 | — | — | — |
| $N_4P_4Cl_7NHPh$ | −6.2; −7.0 | −2.9 | 5.7 | — |
| 6,8-$N_4P_4Cl_6(NHPh)_2$ | −8.6 | −3.0 | 8.0 | 6.7 |
| 4,8-$N_4P_4Cl_6(NHPh)_2$ | — | −3.5 | 6.6 | — |
| Mean value | −7.2 | −3.1 | 6.8 | 6.7 |

*The P–N bond types I, II, III, and IV correspond to isolated P–N bonds in the fragments $Cl_2P–N–PCl_2$, $Cl_2P–NPCl(NHPh)$, $Cl_2PN–PCl(NHPh)$, and (PhNH).ClP–N–PCl(NHPh) respectively.

The observed effect of the nature of substituents on $^1J_{PN}$ enabled us to confirm the change in the sign of $^1J_{PN}$ in relation to the geminal difluoro-derivative $^{15}N_3P_3Cl_4F_2$.[21] For chloro(phenylamino)cyclotetraphosphazenes, it was actually possible to determine directly, by modelling higher-order spectra, the relative sign of $^1J_{PN}$ on the assumption that $^2J_{PP}$ is positive. Thus the signs which we proposed in Table 8 are indeed justified.

It is of interest to compare the influence of substituents on the coupling constants $^1J_{PN}$ for cyclophosphazenes with their influence on the interaction constants $^1J_{CC}$ for monosubstituted benzene derivatives. The constants $^1J_{CC}$ had been determined[97] for C–C bonds occupying different positions in the molecules (see the scheme below) of more than 30 different benzene derivatives.




According to the results of the above study, the maximum changes in the C–C coupling constants for the *a* bond reached 21.3 Hz on passing from R = F to R = $SiH_3$, up to 4.7 Hz for the *b* bond on passing from R = NHMe to R = I, and 1.9 Hz for the *c* bond on passing from R = NCS to R = CHNOH. The coupling constant $^1J_{CC}$ depends on the electro-negativity of the substituent atom linked to the carbon atom.[96] Thus a profound analogy is observed between the changes in the $^1J_{PN}$ for geminally disubstituted cyclotriphosphazenes[21] and the $^1J_{CC}$ for monosubstituted benzene derivatives. The effect of remote substituents on the coupling constants for compounds with ring-delocalised π-systems is weak, in contrast to the influence on the chemical shift of the $^{13}$C signal.

We may note that the endocyclic coupling constants $^3J_{PN}$ are negligible; the exocyclic constants $^3J_{PN}$ for amino-cyclophosphazenes[22,23] will not be considered.

## V. $^{31}$P–$^{31}$P SPIN–SPIN COUPLING CONSTANTS

The coupling constants $^2J_{PP}$ were first determined for chlorofluorocyclotriphosphazenes.[10,11] In many cases the determination of $^2J_{PP}$ was complicated by the additional interactions of the $^{31}$P nuclei with other magnetic nuclei, in the first place protons. The development of the method involving the proton decoupling of the $^{31}$P nuclei was an important step both for the determination of the coupling constants and for the exact determination of the chemical shift $\delta_P$. Numerous constants of this kind are quoted in the literature for cyclotriphosphazenes. The number of such data for cyclotetraphosphazenes is much smaller, since the determination of $^2J_{PP}$ frequently requires model calculations of the spectra. These constants have been determined for certain tetrameric thioethers,[16,37,51,98] ethers,[99] and amino-derivatives.[13,23,100,101]

Analysis of the experimental P–P coupling constants for cyclotriphosphazenes led Finer[102] to the conclusion that $^2J_{PP}$ depends virtually only on the nature of the substituents located about the phosphorus atoms involved in the coupling but is independent of the substituent at the third phosphorus atom. Finer proposed a formula from which it is possible to calculate approximately the P–P coupling constant (in Hz) for any cyclotriphosphazenes:

$$^2J_{PP} = (\lambda_A+\lambda_B)(\lambda_C+\lambda_D). \qquad (7)$$

**Table 11.** Coupling constants $|^2J_{PP}|$ (in Hz) for chloro(ethylthio)cyclotriphosphazenes.

| Compound | Interacting nuclei in fragments | | | | |
|---|---|---|---|---|---|
| | $PCl_2$, $PCl_2$ | $PCl_2$, $PClSEt$ | $PCl_2$, $P(SEt)_2$ | $PClSEt$, $PSEt)_2$ | $P(SEt)_2$, $P(SEt)_2$ |
| $N_3P_3Cl_6$ | 50* | — | — | — | — |
| $N_3P_3Cl_5SEt$ | — | 32.9 | — | — | — |
| $N_3P_3Cl_4(SEt)_2$ | 54.7* | — | 5.0 | — | — |
| $N_3P_3Cl_3(SEt)_3$ | — | 17.3 | 3.5 | 14.1 | — |
| $N_3P_3Cl_2(SEt)_4$ | — | — | 5.2 | — | 17.8* |
| $N_3P_3Cl(SEt)_5$ | — | — | — | 9.9 | — |
| $N_3P_3(SEt)_6$ | — | — | — | — | 14.7* |
| Mean value | 52.4 | 25.1 | 4.6 | 12.0 | 16.3 |
| Calculation by Eqn.(7) | 51.0 | 27.9 | 4.9 | 2.7 | 0.5 |

*Values obtained from spectra of $^{15}$N-labelled compounds.

Here $\lambda_A-\lambda_D$ represents specially selected parameters for the substituents attached to the interacting phosphorus atoms. The values of λ are satisfactorily linearly correlated with the electronegativities of the substituent atoms linked directly to phosphorus. The coupling constants $^2J_{PP}$ can be predicted with a satisfactory accuracy in many cases by means of the Finer formula or the set of values of λ for other substituents can be supplemented.[103–105] Our detailed investigation of the constants $^2J_{PP}$ for hetero-substituted chloro(ethylthio)cyclotriphosphazenes showed that the Finer formula does not lead to correct predictions in all cases (Table 11). Sometimes the values of $^2J_{PP}$ for the same combination of interacting nuclei differ markedly. Judging from the average values quoted in Table 11, $^2J_{PP}$ passes through a minimum as the number of SEt groups

substituting chlorine increases. It is difficult to find a satisfactory explanation of this phenomenon. We therefore suggest that in the above series the sign of $^2J_{PP}$ is reversed after the attainment of the minimum. The Finer formula cannot reflect the above feature.

In the case of substituted 2,2,6,6-tetraethylthiocyclotetraphosphazenes,[16] the sign of $^2J_{PP}$ should also change (Table 12). Indeed, different signs of the P–P coupling constants have been obtained for chloro-2,2-diethylthiocyclotetraphosphazene by model calculations of the $^{31}P$ NMR spectra.[51] The variation of the average constant $^2J_{PP}$ with the degree of substitution for compounds of the type $N_4P_4Cl_{8-n}(SEt)_n$ and $N_3P_3Cl_{6-n}(SEt)_n$ is illustrated in Fig.8. The $^2J_{PP}$ curves for compounds of the trimeric and tetrameric series are parallel if it is assumed that the sign of the constant $^2J_{PP}$ changes on passing from the $PCl_2$–N–$PCl_2$ fragment to the $P(SEt)_2$–N–$P(SEt)_2$ fragment. The above constants for cyclotriphosphazenes are somewhat greater than for cyclotetraphosphazenes. The same tendency has been observed for aminochlorocyclophosphazenes[99] and for chlorophenoxycyclophosphazenes[101] (see also, Sulkowski et al.[106] and Samir et al.[107]).

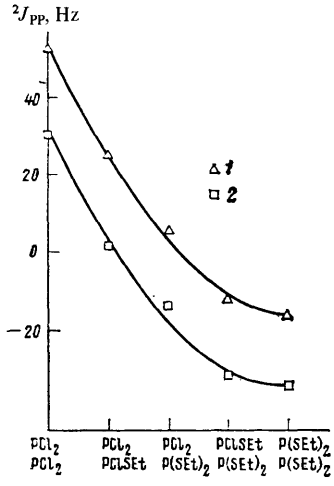



**Figure 8.** Coupling constants $^2J_{PP}$ for cyclotriphosphazenes (1) and cyclotetraphosphazenes (2) with different numbers of Cl and SEt substituents in fragments of the type $R_2PNPR_2$.

**Table 12.** Coupling constants $^2J_{PP}$ for substituted 2,2,6,6-tetraethylthiocyclotetraphosphazenes.

| Interacting nuclei in fragments | $\lvert {}^2J_{PP} \rvert$, Hz | Compound |
|---|---|---|
| $P(SEt)_2$, $P(SEt)_2$ | 31.6* | $N_4P_4(SEt)_8$ |
| $P(SEt)_2$, $P(NH_2)_2$ | 4.0 | $N_4P_4(SEt)_4Cl_2(NH_2)_2$ |
| Ditto | 4.4 | $N_4P_4(SEt)_4(NH_2)_4$ |
| $P(SEt)_2$, $PCl_2$ | 11.8 | $N_4P_4(SEt)_4Cl_4$ |
| Ditto | 11.7 | $N_4P_4(SEt)_4Cl_2(NH_2)_2$ |
| $P(SEt)_2$, PClOEt | 9.6 | *cis*-$N_4P_4(SEt)_4Cl_2(OEt)_2$ |
| Ditto | 10.6 | *trans*-$N_4P_4(SEt)_4Cl_2(OEt)_2$ |
| » | 10.1 | $N_4P_4(SEt)_4Cl(OEt)_3$ |
| $P(SEt)_2$, $P(OEt)_2$ | 18.5 | $N_4P_4(SEt)_4Cl(OEt)_3$ |
| Ditto | 18.5 | $N_4P_4(SEt)_4(OEt)_4$ |
| $P(SEt)_2$, $P(OMe)_2$ | 20.0 | $N_4P_4(SEt)_4(OMe)_4$ |

*Value obtained from the spectrum of a $^{15}N$-labelled compound.

Almost all the P–P coupling constants mentioned hitherto have been obtained for cyclophosphazenes with mixed substituents. The determination of the constant $^2J_{PP}$ for the homosubstituted cyclotriphosphazenes $(NPR_2)_3$ and cyclotetraphosphazenes $(NPR_2)_4$ is possible only when the above compounds contain, apart from phosphorus, other magnetic nuclei with $I = 1/2$, so that higher-order spectra are obtained in which the required constants are reflected. However, Finer et al.[108] were unable to obtain the constants $^2J_{PP}$ from the proton spectra of such compounds by model calculations of the spectra, since the resulting spectra were not sufficiently well resolved.

The possibility of obtaining the P–P coupling constants for $^{15}N$-labelled homosubstituted cyclophosphazenes was already mentioned in the introduction. The graphical method for the determination of these compounds has been discussed in detail.[27,28] The constants are presented in Table 13 but only approximate values of some of them could be obtained, since in the case where the ratio $^2J_{PP}/^1J_{PN}$ is large the spectra do not reflect adequately the required constant.[27,28] The spectra of highly symmetrical compounds contain no information about the relative sign of $^2J_{PP}$ compared with $^1J_{PN}$. The signs listed in Table 13 were selected according to the considerations described above.

**Table 13.** Coupling constants $^2J_{PP}$ (in Hz)* for hexasubstituted cyclotriphosphazenes and octasubstituted cyclotetraphosphazenes.

| Compound | n = 3 | n = 4 |
|---|---|---|
| $(^{15}NPMe_2)_n$ | 4.4 | 10.7 |
| $[^{15}NP(NHMe)_2]_n$ | — | — |
| $[^{15}NP(NHEt_2)]_n$ | — | — |
| $[^{15}NP(NHPh)_2]_n$ | 30–70 | 35–45 |
| $[^{15}NP(NMe_2)_2]_n$ | — | — |
| $[^{15}NP(NEt_2)_2]_n$ | — | — |
| $[^{15}NP(OMe)_2]_n$ | — | 74.3 |
| $[^{15}NP(OEt)_2]_n$ | 90–120 | — |
| $[^{15}NP(OPh)_2]_n$ | — | 80.6 |
| $[^{15}NP(SEt)_2]_n$ | −14.7 | −31.6 |
| $[^{15}NP(SPh)_2]_n$ | −23.5 | — |
| $(^{15}NPF_2)_n$ | 160–180 | 155.0 |
| $(^{15}NPCl_2)_n$ | 45–55 | — |
| $(^{15}NPBr_2)_n$ | (−)4.8 | −27.2 |

*The signs of the constants were not determined experimentally.

Fig. 9 illustrates the dependence of $^2J_{PP}$ for cyclotriphosphazenes and cyclotetraphosphazenes on the electronegativity of the substituent atoms; evidently there is a fairly satisfactory correlation between the values, the straight line for the trimeric compound lying above that for the tetrameric compounds.

Quantum-chemical calculation of these coupling constants in accordance with the $\Delta E$ approximation does not lead to satisfactory results. The Fermi contact contributions to the P–P coupling calculated by Eqn.(6) proved to be smaller approximately by two orders of magnitude than the contributions to the P–N interaction, while the experimental $^2J_{PP}$ and $^1J_{PN}$ coupling constants are mainly of the same order of magnitude. The additional allowance for other contributions (*OD* and *SD*) did not improve appreciably

the agreement between the experimental and calculated data. The approximate method of calculation of the coupling constants is evidently unsuitable for the spin–spin interactions of atoms separated by two bonds.

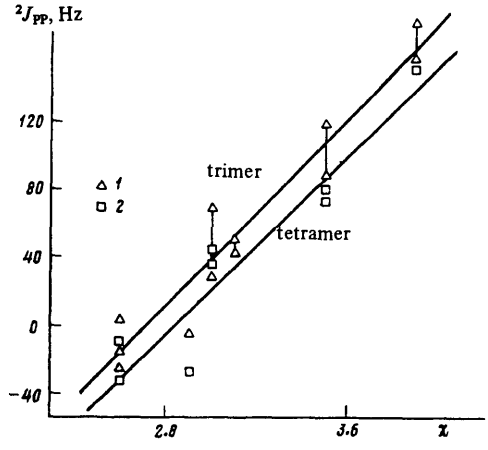



**Figure 9.** Coupling constants $^2J_{PP}$ for hexasubstituted cyclotriphosphazenes (1) and octasubstituted cyclotetraphosphazenes (2) as a function of the electronegativity of the substituent atom.

The coupling constants $^4J_{PP}$ for cyclotetraphosphazenes are small, as might have been expected. Only in certain cases has it been possible to determine them;[99,101,109] the values obtained for the aminochloro-derivatives, chloroethers, and aminoethers are in the range from −0.7 to −2.2 Hz.

## VI. CONCLUSION

The nature of the substituents R at the phosphorus atoms in cyclophosphazenes influences the electronic structure of the $(P-N)_n$ ring as well as the $^{31}P$ and $^{15}N$ chemical shifts and the $^1J_{PN}$ and $^2J_{PP}$ coupling constants. A change in ring size also alters the NMR parameters. A correlation is observed between the electronegativity of the substituent atoms and $\delta_P$ as well as the $^1J_{PN}$ and $^2J_{PP}$ coupling constants, whereas no such correlation exists for $\delta_N$. This has also been confirmed by calculations by the CNDO/2 method, according to which there is a linear correlation between the $\delta_P$ and the part of the paramagnetic contribution which depends on the distribution of electrons, while this type of correlation cannot be traced for $\delta_N$.

In considering the values of the individual parameters, one may reach a number of conclusions. The chemical shift of phosphorus $\delta_P$ depends directly on the nature of the substituents attached to the given phosphorus atom. The substituents at the other phosphorus atoms exert only an insignificant influence on $\delta_P$. Despite this, it is impossible to calculate $\delta_P$ with an adequate accuracy using a system of increments. With increase of ring size, $\delta_P$ undergoes an upfield shift.

The nitrogen chemical shift $\delta_N$ depends on the nature of the substituents at both neighbouring phosphorus atoms, but is independent of the substituents at the more remote phosphorus atoms. In this sense, cyclophosphazenes differ markedly from aromatic compounds with a delocalised π-system. The chemical shift $\delta_N$ varies linearly with the degree of substitution. On passing from trimeric to tetrameric phosphazenes, $\delta_N$ undergoes a downfield shift, while, on further increase of ring size, there is an upfield shift.

The coupling constants $^1J_{PN}$ can be both positive and negative. They depend primarily on the nature of the substituents at the phosphorus atoms involved in the coupling. To a lesser extent, their values are determined by the effect of the substituents at the other phosphorus atom linked to the nitrogen atom considered. The effect of the substituents at the more remote phosphorus atoms has not been observed. With increase of ring size, the constant $^1J_{PN}$ increases. There is an unambiguous relation between $^1J_{PN}$ and the P–N bond length and also the P–N stretching vibration frequency. Semiempirical quantum-chemical calculations have shown that there is a satisfactory correlation between the experimental coupling constants and the Fermi contact contributions. Thus $^1J_{PN}$ is the NMR parameter containing most information from the standpoint of the description of the electronic system of the skeleton of the $(P-N)_n$ rings.

The coupling constants $^2J_{PP}$ can be both positive and negative. They depend mainly on the nature of the substituents at both phosphorus atoms involved in the given coupling and to a lesser extent on the substituents at the other phosphorus atoms. With increase of ring size, $^2J_{PP}$ diminishes.

All the NMR parameters tend to limiting values with increase in ring size.

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# The Physical Chemistry of the Intramolecular Cyclodehydration Reactions of Prepolymers

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The experimental data on the thermodynamics of the intramolecular cyclodehydration reactions of prepolymers in the solid phase are examined and treated systematically. The changes in the thermodynamic functions of the above processes have been analysed in detail over a wide temperature range. The temperature ranges corresponding to the formation of polyheteroarylenes which are "defect-free" to the maximum extent have been estimated.
The bibliography includes 65 references.

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## I. INTRODUCTION

Among the numerous thermostable polymers, the heterocyclochain polymers containing different heterocyclic fragments in the main macromolecular chain are of special importance.

The principal methods of synthesising such polymers involve the polycondensation reactions of di- or tetracarboxylic acids and their derivatives with polyfunctional amines. Polymer macromolecules can then be formed both in one and in several stages.
The diphenyl or dimethyl esters of the corresponding acids and polyamides or their derivatives are usually employed as the initial compounds in polycondensation in the melt; as a result, a heterocyclochain polymer (a polyheteroarylene) is formed in one stage. When the synthesis is carried out in solution, polyamines and free carboxylic acids are as a rule used to obtain polyheteroarylenes in one stage and the solvent is normally polyphosphoric acid.

In the two-stage method of synthesis of polyheteroarylenes, intermediate products, the so-called prepolymers, are obtained in the first stage by the polycondensation of amines or their derivatives with the di-anhydrides (halides) of tetra- or di-carboxylic acids in an amide solvent. The prepolymers are converted in the second stage (thermal cyclisation at 400–650 K at a reduced pressure) into the final product—the heterocyclochain polymers. This polycondensation method is superior to the first two mentioned above. The majority of polyheteroarylenes are insoluble and infusible polymers, because they have a fairly rigid structure; however, in two-stage polycondensation articles can be made from the prepolymer and their heat treatment can impart to them the properties of the final polymer.

This is the explanation of the increasing interest in the thermal cyclodehydration reactions of prepolymers, demonstrated by the large number of publications both in the Soviet Union and abroad. This applies primarily to the study of the kinetics of the solid-phase cyclisation reactions of polyamidoacids.[1-11] The relevant data have been published[12-16] for reactions involving the synthesis of polybenzoxazoles via the intramolecular cyclodehydration of poly(*o*-hydroxyamides). The cyclisation reactions of polyhydrazides in the solid phase have been investigated.[17-22] The quantitative kinetic results and the mechanism of the formation of polybenzimidazoles and polybenzoylenebenzimidazoles have been described by Dawans and Marvel, Izyneer, and Korshak and co-workers[23-29] and by Colson et al, Teleshov et al., Laius et al., and Korshak et al.,[30-33] respectively. In the list quoted above we did not include studies whose results have been discussed in the monographs by Adrova et al.,[34] and Korshak and Vinogradova[35] and also studies devoted to general questions of the synthesis of polyheteroarylenes which have been described in detail in other reviews.[36-39]

In the study of the kinetics of the cyclisation of prepolymers, the vast majority of investigators have used infrared (IR) spectroscopy which makes it possible to follow the process from the change in the intensities of the characteristic absorption bands. Different versions of the same method have been used also to determine the degrees of cyclisation of the final polymers. Information about the IR spectra of various cyclic and heterocyclic molecules can be found in Bellamy's monograph.[40] In the case of polyimides one may employ the book of Adrova et al.,[34] while the paper of Rusanov et al.[41] deals with poly-1,3,4-oxadiazoles; the IR spectra of polybenzoxales have been described by Korshak et al.[42] The IR spectra of other polyheteroarylenes have been described in the original papers dealing with their synthesis.[34,36-39]

Systematic treatment of the available experimental literature data permits the conclusion that the cyclodehydration reactions of prepolymers are intramolecular and in the general case are described by a first-order kinetic equation. They have a number of general kinetic characteristics: (1) the effective rate constants for the cyclisation reactions of prepolymers diminish when the latter are converted into the final polyheteroarylenes and the degree of cyclisation–time isotherms show clearly the instant when the process comes to a stop;[43] (2) with increase of the degree of cyclisation, the activation energies for the above processes increase significantly;[44] (3) with increase of temperature, the limiting degree of cyclisation of the polyheteroarylene also increases.

A number of factors, from which it is possible to interpret the above features of the intramolecular cyclodehydration reactions of prepolymers in the solid phase, have been described in the literature. We shall only note that the majority of investigators attribute the increase of the

activation energy and the decrease of the rate constants for the cyclodehydration process to the increasing rigidity of the polymer chains in this process or, in other words, to the decrease of the number of groups in the polymer unit which are capable of hindered rotation. Here the idea has been put forward that, for kinetic reasons, the reaction involving the synthesis of polyheteroarylenes proceeds at an appreciable rate only in the region of the highly elastic state of the polymer.[25-29]

At the same time, one should note the complete absence of literature data for the thermodynamics of the cyclisation reactions of prepolymers in the solid phase. The authors of this review applied for the first time the classical calorimetric methods to the analysis of these reactions. All this made it possible to determine the enthalpies, entropies, Gibbs free energies, and equilibrium constants for the thermal cyclisation reactions of prepolymers. From our point of view, the results obtained are of undoubted theoretical and applied interest, because they make it possible to predict the average degree of polycondensation and the number-average molecular weight of the polyheteroarylene formed. We therefore believe it essential to survey and treat systematically the experimental data obtained previously for the thermodynamics of the intramolecular cyclodehydration reactions of a number of prepolymers.

## II. THERMODYNAMICS OF THE INTRAMOLECULAR CYCLODEHYDRATION REACTIONS OF PREPOLYMERS

This Section deals with the results obtained in the study of the thermodynamics of the synthesis of a series of polyheteroarylenes via the intramolecular cyclodehydration of the corresponding prepolymers.

The general approach to the solution of the problem was as follows. A study was made of the heat capacity $C_p^0$ of the prepolymers and the corresponding polyheteroarylenes in the temperature range 60–650 K. For this purpose, use was made of the adiabatic calorimeters described in detail by Lebedev and Lityagov.[45] The accuracy of the heat capacities of the polymers obtained was to within 0.2–0.3% in the temperature range 60–300 K, to within 0.7–1.0% in the range 300–500 K, and 1.5% at higher temperatures. Extrapolation of the experimental curves for the heat capacities of the prepolymers from 60 to 0 K was carried out in terms of the two-parameter Tarasov equation:[46,47]

$$C_p^0(1,3) = K\left\{D_1\left(\frac{\Theta_1}{T}\right) - \left(\frac{\Theta_3}{\Theta_1}\right)\left[D_1\left(\frac{\Theta_3}{T}\right) - D_3\left(\frac{\Theta_3}{T}\right)\right]\right\}, \quad (1)$$

where $\Theta_1$ and $\Theta_3$ are the characteristic temperatures, $D_1$ and $D_3$ the Debye functions of the heat capacities of the one-dimensional and three-dimensional continua, and $K$ is a constant coefficient for the given polymer.

The Kelley–Parks–Huffman extrapolation method was employed for the polyheteroarylenes:[48]

$$C_p^0 = (a + bT) \cdot C_p^0\,(\mathrm{PP}),$$

where $C_p^0$ is the heat capacity of the given polyheteroarylene, $C_p^0$ (PP) the heat capacity of the corresponding prepolymer at the same temperatures, and $a$ and $b$ are empirically selected constants.

The coefficients and characteristic temperatures were chosen such that the heat capacities calculated from the corresponding equation do not differ from the experimental values of $C_p^0$ in the range 60–80 K by more than 0.3%. The thermodynamic functions of the polymers were calculated from the equations

$$H^0(T) - H^0(0) = \int_0^T C_p^0\,\mathrm{d}T;\ S^0(T) - S^0(0) = \int_0^T C_p^0\,\mathrm{d}\ln T;$$
$$G^0(T) - H^0(0) = [H^0(T) - H^0(0)] - T\,[S^0(T) - S^0(0)]\ . \quad (2)$$

The integrals were calculated by Simpson's method[49] or with the aid of a computer. As mentioned above, the reactions leading to the synthesis of polyheteroarylenes by intramolecular cyclodehydration of the prepolymer are carried out in the solid phase and are accompanied by a considerable increase of the rigidity of the macromolecular chain. They hardly ever go to completion and the polyheteroarylene formed is a heterounit polymer containing the structural fragments of the prepolymer in its composition. This factor leads to the necessity for the determination of the degree of cyclisation of the prepolymer (the extent to which the polyheteroarylenes have a heterounit structure). The method employed for this purpose[50,51] is based on the additivity of the enthalpies of combustion of the statistical copolymers relative to the corresponding homopolymers:[52]

$$M_2'\Delta h_c^0(298,\ \mathrm{PHA}) = N_2\Delta H_c^0(298,\ \mathrm{PHA}) + (1 - N_2)\,\Delta H_c^0(298,\ \mathrm{PP}), \quad (3)$$

where $M_2' = N_2M_2 + (1 - N_2)M_1$ is the average molecular weight of the repeat unit of the real polyheteroarylene specimen, $N_2$ the mole fraction of the heterocycles in the polyheteroarylene specimen investigated, and $M_1$ and $M_2$ are the molecular weights of the prepolymer units and the polyheteroarylene respectively; $\Delta H_C^0$ (298, PP) and $\Delta H_C^0$ (298, PHA) are the standard enthalpies of combustion of the prepolymer and the ideal 100% polyheteroarylene at 298.15 K respectively and $\Delta h_C^0$ (298, PHA) is the standard specific enthalpy of combustion of the real polyheteroarylene specimen at 298.15 K. Eqn.(3) can be written in the following form

$$[N_2M_2 + (1 - N_2)\,M_1]\,\Delta h_c^0(298,\ \mathrm{PHA}) = N_2\Delta H_c^0(298,\ \mathrm{PHA}) + (1 - N_2)\,\Delta H_c^0(298,\ \mathrm{PP}).$$

Bearing in mind that $\Delta H_C^0$ (298, PP) − $\Delta H_C^0$ (298, PHA) = $\Delta H_r^0$ (298) is the enthalpy of cyclisation of the prepolymer at 298.15 K, we obtain

$$N_2 = [\Delta H_c^0(298,\ \mathrm{PP}) - M_1\Delta h_c^0(298,\mathrm{PHA})]/[\Delta h_c^0(298,\ \mathrm{PHA})(M_2 - M_1) + \Delta H_r^0(298)]\ . \quad (4)$$

The quantity $\Delta h_C^0$ (298, PHA) was determined experimentally in an isothermal bomb calorimeter at 298.15 K under standardised combustion conditions. A V-08 calorimeter[53] was used for this purpose; twice the standard deviation of the quantities obtained did not exceed 0.1%.

The $\Delta H_C^0$ (298, PP) were calculated from the experimental enthalpy of formation of the prepolymer in solution taking into account the enthalpies of solution of the starting materials and the polymer as well as the standard enthalpies of combustion of the monomers. Compared with the method based on the direct combustion of the prepolymer, this procedure for the determination of $\Delta H_C^0$ (298, PP) can eliminate the influence of the possible presence of the solvent in the polymer on the enthalpy of combustion of the prepolymer being determined.

The equilibrium water vapour pressure over the prepolymer in the course of its cyclisation reaction was used to determine the enthalpy of cyclodehydration. The tensimetric version of the static method was selected.[54] The absolute values of the measured water vapour pressure in duplicate experiments differed by not more than (1–2) × $10^{-1}$ kPa, which led to an error in the determination of the enthalpies of cyclodehydration of the prepolymers not exceeding ±2.0 kJ mol$^{-1}$.

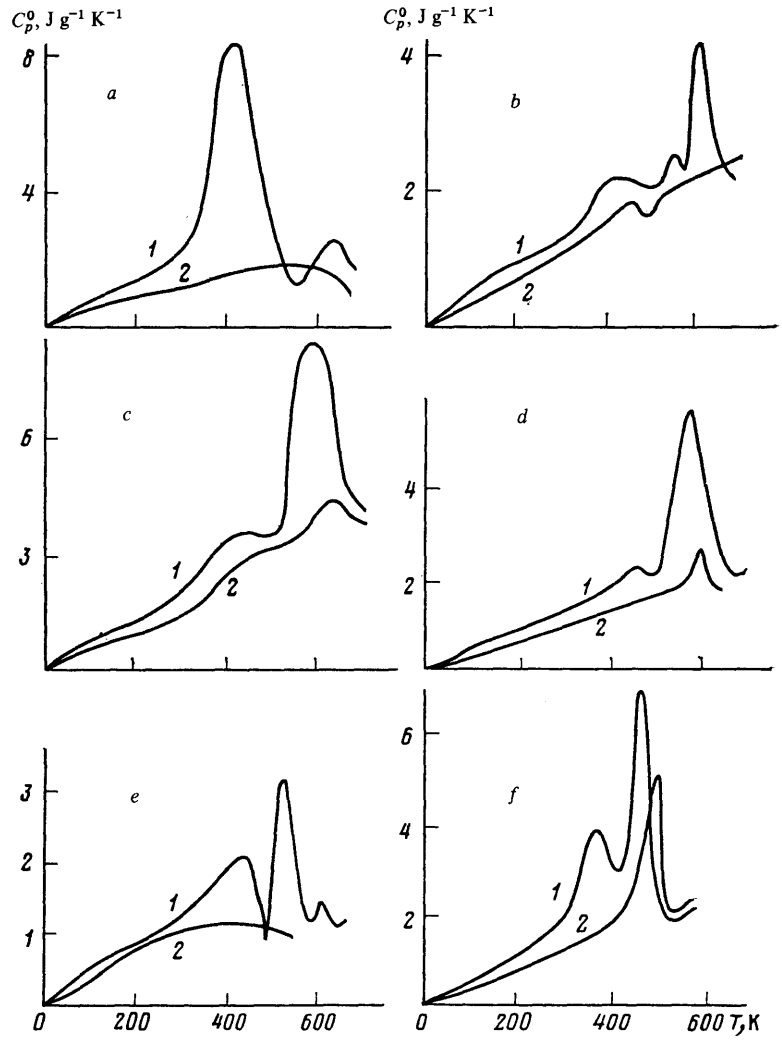



**Figure 1.** Temperature variation of the specific heats: *a*) of the polyamidoacid (PAA, curve *1*) and poly(*pp'*-diphenyl oxide)pyromellitimide (PI, curve *2*);[55] *b*) of poly(*o*-amido)-1,2,4-triazole (PATA, curve *1*) and polytriazoloquinazoline (PTAQ, curve *2*);[56] *c*) of poly(*o*-aminophenyl)benzimidazole (PBA, curve *1*) and polybenzimidazoloquinazoline (PBIQ, curve *2*);[62] *d*) of poly(*pp'*-diphenylphthalide)hydrazide (PH-P, curve *1*) and poly(*pp'*-diphenylphthalide)-1,3,4-oxadiazole (POD-P, curve *2*);[57] *e*) of poly(*pp'*-diphenyl oxide)hydrazide (PH-O, curve *1*) and poly(*pp'*diphenyl oxide)-1,3,4-oxadiazole (POD-O, curve *2*);[58] f) of poly(4,4'-dihydroxy-3,3'-isophthalamidodiphenylmethane) (POA, curve *1*) and poly[2,2'-(*m*-phenylene)-5,5'-dibenzoxazolymethane (PBO, curve *2*).[59]

→αβωε [6~]

In most cases the vapour phase was analysed chromatographically to determine the possible content of the corresponding solvent. For the given heterogeneous reaction, the equilibrium constant is determined by the expression $K_p = P^n(H_2O)$, where $n$ is the number of moles of water evolved in the cyclisation of the prepolymer per repeat unit. The equation of the reaction isobar can therefore be expressed as $d \ln P^n/dT = \Delta H_p/RT^2$; when the integration is carried out in terms of the approximation that $\Delta H_P$ is independent of $T$ over a narrow temperature range, this expression yields $n \ln P = -\Delta Hp/RT + C$, i.e. a linear relation between $\ln P$ and $1/T$. In view of this, the enthalpy of cyclodehydration $\Delta H_r^0(T)$ at a certain average temperature $T$ in the experimental temperature range was determined from the plot of the linear relation $\ln P = f(T^{-1})$. The same quantity at $T = 298.15$ K was calculated from the Kirchhoff formula taking into account the heat capacities of the polymer and water. (It has been established[55] that the heat capacities of polyheteroarylene specimens with a high degree of cyclisation differ little from the heat capacity of the corresponding 100% polyheteroarylene).

The heat capacities and thermodynamic functions of 100% polyheteroarylenes were calculated from the thermodynamic properties of real polyheteroarylene specimens and the known degree of their heterounit structure assuming additivity. For example, the entropy of 100% polyheteroarylene at the given temperature is defined by the relations

$$M_2'S^0(\text{PHA}) = N_2S_M^0(\text{PHA}) + (1 - N_2)S^0(\text{PP}); \quad (5)$$
$$S_M^0(\text{PHA}) = \{[N_2M_2 + (1 - N_2)M_1]S^0(\text{PHA}) - (1 - N_2)'S^0(\text{PP})\}N_2^{-1},$$

where $S^0$(PHA) is the specific entropy of the polyheteroarylene investigated at the given temperature, $S^0_m$(PHA) the molar entropy of the 100% polyheteroarylene, and $S^0$(PP) the molar entropy of the prepolymer at this temperature.

The entropies of cyclodehydration at each temperature were calculated from the entropies of the reactants. The zero-point entropy of the polymer, which is not taken into account in the given instance, introduce a small error into the determination of the entropy of reaction, because the difference between the zero-point entropies of polyheteroarylene and the corresponding prepolymer is comparatively small.

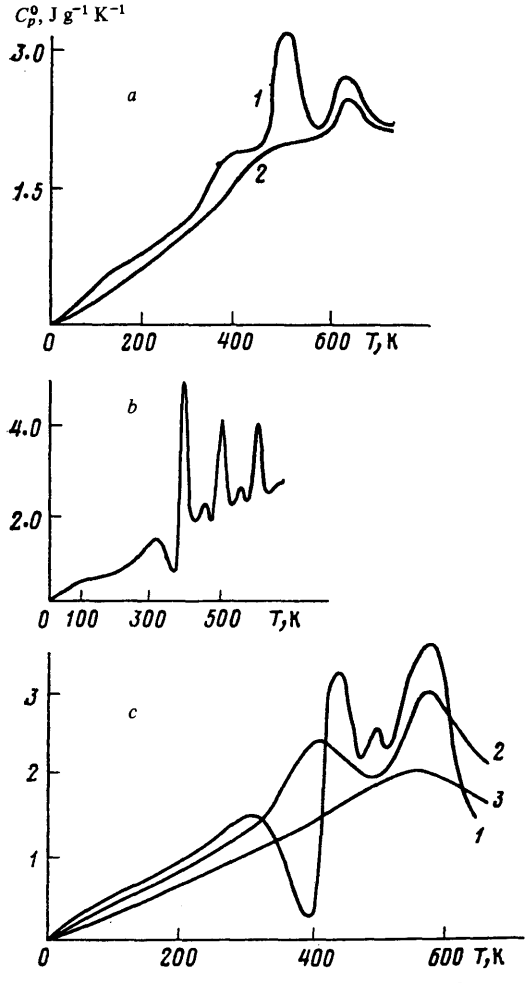



**Figure 2.** Temperature variation of the specific heats: *a*) of poly[*N*-terephthaloylbis(*N'*-phenyl-*o*-diphenylamine)] (PPDA, curve *1*) and poly[2,2'-(*p*-phenylene)-1,1'-diphenyl-5,5'-dibenzimidazole] (PPDBA, curve *2*);[60] *b*) of polyaminoamidoacid (PAAA);[50] *c*) of poly(*o*-carboxy) benzoylamidrazone (PCBA, curve *1*), polyamidinoimide (PADI, curve *2*), and polybenzoylene-*s*-triazole (PBTA, curve *3*).[63]

The Gibbs free energy of cyclodehydration at each temperature was calculated by the Gibbs–Helmholtz equation from the enthalpies $\Delta H^0_r(T)$ and entropies $\Delta S^0_r(T)$ obtained. The equilibrium constant was calculated from the equation of the reaction isotherm: $\Delta G^0_r(T) = -RT \ln Kp$.

## III. THE HEAT CAPACITIES OF PREPOLYMERS AND POLYHETEROARYLENES

In the range 60–300 K the heat capacities of prepolymers and polyheteroarylenes increase monotonically with increase of temperature. As a consequence of the greater rigidity of the macromolecular chain of polyheteroarylenes, their heat capacities are always smaller than the corresponding $C^0_p$ for the prepolymers at the same temperatures. At higher temperatures the curves representing the temperature variation of the heat capacities of the prepolymers investigated exhibit distinct anomalies in the form of endothermic peaks. These anomalies are associated with the intramolecular cyclodehydration reactions of the prepolymers.

In most cases a single peak is observed:[55–63] in the temperature ranges 350–550 K (PAA, Fig.1*a*), 550–650 K (PATA, Fig.1*b*), 550–650 K (PBA, Fig.1*c*), 520–600 K (PH-P, Fig.1*d*), 500–560 K (PH-O, Fig.1*e*), and 450–520 K (POA, Fig.1*f*). The curves for the temperature dependence of the heat capacities of the other prepolymers investigated have two (PPDA, Fig.2*a*) and even three endothermic peaks (PAAA, Fig.2*b*, and PCBA, Fig.2*c*). In many instances, the appearance of the endothermic peak is preceded by a jump in heat capacity due to the devitrification of the initial prepolymer in the temperature ranges 352–420 K (PATA, Fig.1*b*), 380–450 K (PBA, Fig.1*c*), ~510 K (PH-P, Fig.1*d*), 400–450 K (PH-O, Fig.1*e*), 280–350 K (PAAA, Fig.2*b*), and 350–400 K (PPDA, Fig.2*a*).

In view of this, one can assume that the intramolecular cyclodehydration reactions in general actually occur at temperatures above the glass point of the corresponding prepolymer, where there is a sharp increase of the mobility of the polymer segments. Precisely under these conditions, the kinetic energy of the polymer units can exceed the energy of the activation barrier to the reaction and there is a possibility that a transition state may be formed. The occurrence of cyclodehydration in several stages can be accounted for in the same way, i.e. by kinetic causes. For example, in the reaction involving PAAA (Fig.3*b*), two water molecules are split off from the repeat unit of the polymer in the first stage at ~410 K with formation of polyamidoimide (PAI).

It is easy to suppose that the activation energy for the reaction PAA → PAI + $2H_2O$ is appreciably lower than the activation energy for the simultaneous elimination from the polyamidoacid unit of four water molecules with formation of polybenzoylenebenzimidazole (PAAA → PBBA + $4H_2O$). It was more difficult to explain why the elimination of two water molecules from the polyamidoimide unit with its conversion into a polybenzoylenebenzimidazole unit (PAI → PBBA + $2H_2O$) and also the elimination of two water molecules from the polyamidinoamide unit with its conversion into polybenzoylene-*s*-triazole (PADI → PBTA + $2H_2O$) or of two water molecules from the poly[*N*-terephthaloylbis(*N'*-phenyl-*o*-diphenylamine)] via the reaction PPDA → PPDBA + $2H_2O$ proceeds in two stages. We suggest that these are not two different processes or two stages of an overall process but one and the same process occurring partly in one temperature range and partly in another. The point is that, when the cyclodehydration reaction of the prepolymer cannot occur, for kinetic reasons, at a realistic rate at a temperature corresponding to the vitreous state of the polymer, it begins only after the system has been heated above the devitrification temperature. However, having

begun, the process itself leads to an increase of the rigidity of the polymer chain and hence to an increase of the glass point. For this reason, whereas at the beginning of the process, when the system is heated, the devitrification of the polymer due to the increase of temperature predominates over the vitrification process due to the increased fraction of cyclic fragments in the polymer as a consequence of the cyclodehydration reaction, after the attainment of a certain degree of conversion of the prepolymer into the final heterocycle, the relative contributions of the above processes are reversed, which leads to the arrest of cyclisation. However, on further increase of temperature, whereupon the polymer again passes to the highly elastic state, the cyclodehydration process continues. From this standpoint, the difference between the thermodynamic and kinetic parameters of the individual stages of the reaction can be accounted for by the different rigidities of the polymer chains and by the different interchain interaction energies in these stages and also directly by the difference between the temperatures of both ranges where the given processes take place.

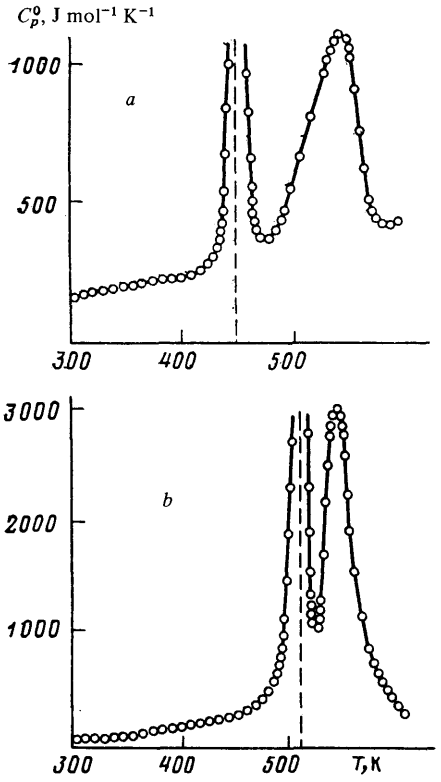
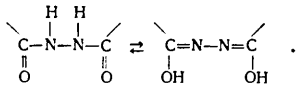
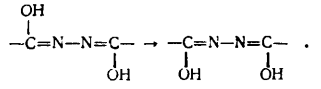



**Figure 3.** Temperature variation of the heat capacities of the *NN'*-dibenzoylhydrazide of diphenylphthalide-4,4'-dicarboxylic acid (*a*) and the *NN'*-dibenzoylhydrazide of (diphenyl oxide)-4,4'-dicarboxylic acid (*b*).[63]

If the rigidity of the polymer chain plays an important role in prepolymer cyclodehydration processes, their occurrence should depend significantly on the initial structure of the polymer. The authors of this review therefore carried out a comparative study of the cyclodehydration reactions of polyhydrazides and their low-molecular-weight analogues of different structure. It has been suggested[64] that the occurrence of the cyclodehydration of polyhydrazides is associated with the formation of a transition state in the system whose conformation is close to that of the *cis*-form of the hydrazide fragment:



At the same time, analysis of three-dimensional models and conformational calculations for chains of analogous structure[64] have shown that, from the standpoint of the interchain interaction and packing effects in the solid polymer, the *trans*-form of the hydrazide fragment is the most favourable. In view of this, the formation of the transition state is preceded by the rotational isomerisation of the hydrazide group:



Consequently the composition and structure of the initial polyhydrazide should have a significant influence on the tendency of the hydrazide groups towards intramolecular cyclodehydration, because the chemical nature of the fragments determines the initial flexibility of the polyhydrazide chain.

For comparative analysis, Karyakin[63] investigated poly-2,5-(*pp'*-diphenyl oxide hydrazide) (PH-O), poly-2,5-(*pp'*-diphenylphthalyl hydrazide) (PH-P), and their low-molecular-weight analogues: *NN'*-dibenzoylhydrazide of diphenylphthalide 4,4'-dicarboxylic acie (M-P) and *NN'*dibenzoylhydrazide of (diphenyl oxide)-4,4'-dicarboxylic acid (M-O).

It follows from Fig. 3 that the heat capacity of M-P increases monotonically with increase of temperature from 300 to 420 K. At 450 K M-P crystals begin to melt. In the range 460–560 K (the maximum heat capacity is observed at 530 K) a second endothermic peak, associated with the cyclodehydration of M-P and its conversion into the corresponding cyclic compound, appears. An analogous picture is observed also for M-O (Fig. 3*b*). The endothermic peak in the range 520 to 580 K (the temperature of the maximum is 530 K), due to the cyclodehydration of M-O, is preceded by the fusion of the polymer at 510 K. Thus one may conclude that the thermal cyclodehydration of the model compounds M-O and M-P with formation of the corresponding 1,3,4-oxadiazoles takes place at an appreciable rate only in the melt of the initial hydrazide. With increase of the rigidity of the molecules of the model compound M-P compared with that of M-O, both the temperature range of the cyclodehydration reaction and the range between the melting point and the temperature of the maximum rate of cyclisation is observed.

Accordingly, the introduction of the bulky phthalide group into the polymer chain, which increases the rigidity of the chain and diminishes thereby the number of groups in the polyhydrazide unit capable of internal rotation, leads, firstly, to an incrase of the glass point of PH-P compared with PH-O (510 and 440 K respectively) and, secondly, increases the cyclodehydration temperature (which is higher by ~50 K for PH-P than for PH-O). An analogous effect is observed also on comparing the temperature variations of the heat capacities of the heterounit PH-P, the degree of cyclisation of which is 0.5, and the uncyclised PH-P. The increase of the rigidity of the system in the former case entails an increase of the glass point and of the temperature of the onset of cyclodehydration.[63]

## IV. THE WATER VAPOUR PRESSURES OVER THE PREPOLYMERS IN THE COURSE OF THEIR CYCLODEHYDRATION

In order to calculate the enthalpies of the intramolecular cyclodehydration of the prepolymers, a study was made of the equilibrium vapour pressure of water over the corresponding polymers during their cyclisation.[55-63] The data obtained are fully consistent with the above conclusions concerning the character of the solid-phase cyclisation reactions. As an illustration, Fig. 4 presents such data for a polyaminoamidoacid and poly[*N*-terephthaloylbis(*N'*-phenyl-*o*-diphenylamine)]. The cyclodehydration of the polyaminoamidoacid (Fig. 4*a*) takes place in three stages: the elimination of two water molecules with conversion into PAI (curve *1*) and the subsequent elimination of two water molecules with conversion of the PAI units into PBBA [poly(benzoylene)benzimidazole - Ed. of translation] units. The cyclodehydration of PPDA (Fig. 4*f*) takes place in two stages, in each of which two water molecules are split off from the repeat unit of the initial polymer with formation of PPDBA.

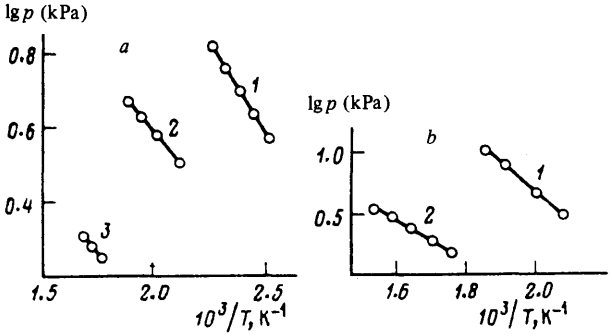



**Figure 4.** Temperature variation of the water vapour pressures over PAAA[50] (*a*) and PPDA[60] (*b*) in the course of their cyclisation: 1)–3) successive water elimination stages in the reactions.

Table 1 lists the coefficients of the corresponding equations $\lg p = f(T^{-1})$, which describe the experimental water vapour pressures over a series of prepolymers. Table 2 presents the results of the determination of the degrees of cyclisation of various polyheteroarylenes by Eqn. (4). Evidently, the polyheteroarylenes investigated are indeed heterounit polymers whose composition includes also the uncyclised units of the initial prepolymer.

## V. ANALYSIS OF THE THERMODYNAMIC CHARACTERISTICS

The data on the thermodynamic properties of the prepolymers and the corresponding polyheteroarylenes described above have been used to calculate the standard enthalpies, entropies, and Gibbs free energies (Table 3). Analysis of the results permits a conventional subdivision of all the prepolymers investigated into two groups (Table 4). $\Delta H_r^0(T) < 0$ is observed at temperatures in the range 100–300 K for the group I prepolymers (PAAA, PCBA, PAA, PAI, PADI, and POA), while $\Delta H_r^0(T) > 0$ occurs at the same temperature for the group II prepolymers (PH-P, PBA, PATA, and PPDA). Above 373 K, the enthalpies of cyclodehydration are positive for polymers of both groups which is caused mainly by the elimination of water in the vapour state. Under these conditions, $\Delta H_r^0(400)$ for the group I prepolymers is lower than for those in group II (Table 4).

**Table 1.** The coefficients of the equations $\lg p = A - B/T$ (the pressures $p$ are expressed in kPa).

| Prepolymer | *T*, K | *A* | *B* | Refs. |
|---|---|---|---|---|
| PAA | 380—440 | 5.000±0.045 | 1668±20 | [55] |
| PAAA | 400—440 | 3.301±0.004 | 1097±40 | |
| | 470—530 | 1.909±0.007 | 655±20 | [50, 63] |
| | 570—590 | 1.055±0.003 | 444±15 | |
| PCBA | 365—423 | 2.416±0.075 | 668±30 | |
| | 450—480 | 2.605±0.008 | 904±10 | [63] |
| | 485—548 | 5.121±0.344 | 2012±40 | |
| POA | 460—515 | 5.524±0.016 | 1945±5 | [59] |
| PH-P | 430—490 | 6.862±0.018 | 3237±8 | [57] |
| PH-O | 470—550 | 7.082±0.334 | 3205±30 | [58] |
| PPDA | 480—540 | 6.614±0.055 | 2959±28 | [60] |
| | 570—650 | 3.701±0.021 | 2103±3 | |
| PATA | 520—580 | 6.617±0.013 | 2750±3 | [56] |
| PBA | 460—540 | 5.900±0.240 | 2650±80 | [62] |

**Table 2.** Experimental degrees of cyclisation ($N_2$) of polyheteroarylenes*.

| Prepolymer | Final polymer | $-\Delta H_c^0$ (298, PP) kJ mol$^{-1}$ | $-\Delta h_c^0$ (298, FP) kJ g$^{-1}$ | $\Delta H_r^0$ (298), kJ mol$^{-1}$ | $N_2$ | Refs. |
|---|---|---|---|---|---|---|
| PAA | PI | 9619±9 | 25.05±0.05 | −6.5±1.0 | 0.96 | [55] |
| PAAA | PAI | 12940±16 | 25.38±0.03 | −45.0±1.0 | 0.89 | [50] |
| PAI | PBBA | 12895±20 | 27.00±0.03 | −56.0±2.0 | 0.71 | [50] |
| PCBA | PADI | 11072±10 | 23.37±0.03 | −77.5±1.5 | 0.88 | [63] |
| PADI | PBTA | 10995±11 | 25.15±0.05 | −6.0±0.5 | 0.82 | [63] |
| POA | PBO | 10161±14 | 30.92±0.04 | −3.0±1.0 | 0.88 | [59] |
| PH-P | POD-P | 14125±12 | 28.47±0.03 | 40.2±1.0 | 0.97 | [57] |
| PH-O | POD-O | 6353±7 | 26.95±0.02 | 28.5±2.0 | 0.97 | [58] |
| PPDA | PPDBA | 16134±18 | 34.75±0.03 | 22.0±2.0 | 0.88 | [60] |
| PATA | PTAQ | 14862±15 | 30.31±0.02 | 34.3±1.0 | 0.92 | [56] |
| PBA | PBIQ | 16387±10 | 31.03±0.03 | 31.0±3.0 | 0.93 | [62] |

Notation: $\Delta H_c^0$(298, PP) is the enthalpy of combustion of the prepolymer, $\Delta h_c^0$(298, FP) the specific enthalpy of combustion of the final polyheteroarylene, and $\Delta H_r^0$(298) the enthalpy of cyclisation of the prepolymer.

In terms of the sign and the absolute order of magnitude, the entropies of cyclodehydration are the same for both groups of prepolymers, because the entropies of the final and intermediate polymers do not differ greatly and the quantity $\Delta S_r^0(T)$ is mainly determined by the entropy of two moles of water.

**Table 3.** Thermodynamic characteristics of the intramolecular solid-phase cyclodehydration of a series of prepolymers at atmospheric pressure.

| $T$, K | $-\Delta H_r^0(T)$ kJ mol$^{-1}$ | $\Delta S_r^0(T)$, J mol$^{-1}$ K$^{-1}$ | $-\Delta G_r^0(T)$, kJ mol$^{-1}$ | $-\Delta H_r^0(T)$ kJ mol$^{-1}$ | $\Delta S_r^0(T)$, J mol$^{-1}$ K$^{-1}$ | $-\Delta G_r^0(T)$, kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|
| PAAA(s) → PAI(s) + 2H$_2$O(s) (Ref.63) | | | | PAI(s) → PBBA(s) + 2H$_2$O(s) (Ref.63) | | |
| 100 | 52.5 | 22.0 | 54.5 | 85.0 | —60.0 | 79.0 |
| 150 | 53.5 | 9.0 | 55.0 | 85.5 | —65.5 | 75.5 |
| 200 | 54.5 | 4.0 | 55.0 | 88.5 | —71.5 | 74.0 |
| 250 | 56.0 | —2.0 | 55.5 | 88.5 | —81.0 | 68.0 |
| PAAA(s) → PAI(s) + 2H$_2$O(l) | | | | PAI(s) → PBBA(s) + 2H$_2$O(l) | | |
| 298.15 | 45.0 | 38.0 | 56.0 | 56.0 | —39.0 | 44.4 |
| 350 | 42.0 | 45.5 | 58.0 | 62.5 | —42.0 | 48.0 |
| PAA(s) → PAI(s) + 2H$_2$O(g) | | | | PAI(s) → PBBA(s) + 2H$_2$O(g) | | |
| 400 | —42.0 | 270.0 | 66.0 | —21.0 | 165.5 | 45.0 |
| PCBA(s) → PADI(s) + 2H$_2$O(s) (Ref.63) | | | | PADI(s) → PBTA(s) + 2H$_2$O(s) (Ref.63) | | |
| 100 | 89.0 | —4.00 | 88.5 | —19.0 | —4.50 | 18.5 |
| 150 | 89.5 | —9.00 | 88.0 | —19.0 | —6.00 | 18.0 |
| 200 | 90.5 | —13.5 | 88.0 | —19.5 | —6.50 | 18.0 |
| 250 | 91.0 | —17.0 | 86.5 | —19.5 | —6.00 | 18.0 |
| PCBA(s) → PADI(s) + 2H$_2$O(l) | | | | PADI(s) → PBTA(s) + 2H$_2$O(l) | | |
| 298.15 | 77.5 | 33.5 | 87.5 | —6.00 | 42.0 | 18.5 |
| 350 | 71.5 | 54.5 | 90.5 | 8.50 | 67.0 | 15.0 |
| PCBA(s) → PADI(s) + 2H$_2$O(g) | | | | PADI(s) → PBTA(s) + 2H$_2$O(g) | | |
| 400 | —25.5 | 307.5 | 97.5 | 74.5 | 230.0 | 17.5 |
| PAAA(s) → PBBA(s) + 4H$_2$O(s) | | | | PCBA(s) → PBTA(s) + 4H$_2$O(s) | | |
| 100 | 137.5 | —38.0 | 133.5 | 108.0 | —8.50 | 107.0 |
| 150 | 139.0 | —56.5 | 130.5 | 108.5 | —14.5 | 106.0 |
| 200 | 143.0 | —67.5 | 129.0 | 110.0 | —20.0 | 106.0 |
| 250 | 144.5 | —83.0 | 123.5 | 110.5 | —23.0 | 104.5 |
| PAAA(s) → PBBA(s) + 4H$_2$O(l) | | | | PCBA(s) → PBTA(s) + 4H$_2$O(l) | | |
| 298.15 | 101.0 | —1.00 | 100.5 | 83.5 | 75.5 | 106.0 |
| 350 | 104.5 | 3.50 | 106.0 | 63.0 | 121.5 | 105.5 |
| PAAA(s) → PBBA(s) + 4H$_2$O(g) | | | | PCBA(s) → PBTA(s) + 4H$_2$O(g) | | |
| 400 | —63.0 | 435.5 | 111.0 | —100.0 | 538.0 | 115.0 |
| PAA(s) → PI(s) + 2H$_2$O(s) (Ref.55) | | | | POA(s) → PBO(s) + 2H$_2$O(s) (Ref.59) | | |
| 100 | —12.0 | —8.50 | 11.0 | —8.00 | —6.50 | 7.50 |
| 150 | —13.5 | —20.5 | 10.5 | —11.5 | —12.0 | 9.50 |
| 200 | —15.0 | —31.0 | 9.00 | —12.5 | —19.0 | 8.50 |
| 250 | —17.0 | —39.0 | 7.00 | —14.5 | —26.5 | 8.00 |
| PAA(s) → PI(s) + 2H$_2$O(l) | | | | POA(s) → PBO(s) + 2H$_2$O(l) | | |
| 298.15 | —6.50 | 25.0 | 14.5 | —3.00 | 13.5 | 7.00 |
| 350 | —6.50 | 33.5 | 18.0 | —2.50 | 12.0 | 5.50 |
| PAA(s) → PI(s) + 2H$_2$O(g) | | | | POA(s) → PBO(s) + 2H$_2$O(g) | | |
| 400 | 67.0 | 232.0 | 26.0 | 79.0 | 225.0 | 11.0 |
| 410 | 64.0 | 226.0 | 28.5 | | | |
| 450 | | | | 78.0 | 216.5 | 19.5 |
| 490 | | | | 74.5 | 210.5 | 28.5 |
| PH-P(s) → POD-P(s) + 2H$_2$O(s) (Ref.57) | | | | PATA(s) → PTAQ(s) + 2H$_2$O(s) (Ref.56) | | |
| 100 | 23.0 | 21.5 | 21.0 | 19.0 | —1.00 | 19.0 |
| 150 | 23.5 | 27.5 | 19.5 | 19.5 | 0.00 | 19.5 |
| 200 | 24.0 | 31.5 | 17.5 | 19.5 | 1.50 | 19.0 |
| 250 | 25.0 | 34.0 | 16.5 | 20.5 | 4.00 | 19.5 |
| PH-P(s) → POD-P(s) + 2H$_2$O(l) | | | | PATA(s) → PTAQ(s) + 2H$_2$O(l) | | |
| 298.15 | 39.5 | 94.0 | 11.5 | 34.5 | 58.5 | 17.0 |
| 350 | 40.5 | 96.0 | 7.00 | 41.0 | 71.0 | 16.0 |
| PH-P(s) → POD-P(s) + 2H$_2$O(g) | | | | PATA(s) → PTAQ(s) + 2H$_2$O(g) | | |
| 400 | 124.0 | 300.0 | 4.00 | 122.0 | 288.5 | 6.50 |
| 450 | 123.0 | 300.0 | —12.0 | 118.0 | 280.5 | —8.00 |
| 500 | 122.0 | 290.0 | —23.0 | 114.0 | 265.5 | —19.0 |
| 550 | — | — | — | 105.5 | 255.0 | —35.0 |
| PBA(s) → PBIQ(s) + 2H$_2$O(s) (Ref.62) | | | | PPDA(s) → PPDBA(s) + 2H$_2$O(s) (Ref.60) | | |
| 100 | 28.5 | —3.50 | 29.0 | 9.00 | —45.0 | 13.5 |
| 150 | 26.5 | —18.0 | 29.0 | 8.50 | —48.5 | 16.0 |
| 200 | 24.5 | —31.0 | 30.5 | 8.00 | —51.0 | 18.0 |
| 250 | 21.5 | —45.0 | 32.5 | 8.00 | —52.0 | 21.0 |
| PBA(s) → PBIQ(s) + 2H$_2$O(l) | | | | PPDA(s) → PPDBA(s) + 2H$_2$O(l) | | |
| 298.15 | 31.0 | —9.00 | 33.5 | 22.0 | 0.50 | 22.0 |
| 350 | 31.5 | —7.75 | 34.0 | 25.0 | 8.50 | 22.0 |
| PBA(s) → PBIQ(s) + 2H$_2$O(g) | | | | PPDA(s) → PPDBA(s) + 2H$_2$O(g) | | |
| 400 | 111.5 | 217.5 | 24.5 | 102.5 | 215.5 | 16.5 |
| 450 | 106.0 | 206.5 | 13.0 | 100.5 | 209.0 | 6.50 |
| 500 | 101.5 | 191.0 | 6.00 | 100.5 | 209.0 | —4.00 |
| 550 | 85.5 | 167.0 | —6.50 | 97.0 | 201.0 | —13.5 |
| 600 | 72.0 | 144.0 | —14.5 | | | |

The free energy $\Delta G_r^0(T)$ for the group I prepolymer is negative at all temperatures, because at low temperatures (100–300 K) the cyclodehydration processes are exothermic and their entropies are either small and negative or (usually) positive. At higher temperatures ($T \geq 400$ K) the enthalpies of these reactions are in all cases positive, but they are characterised by large positive entropies (Table 5), so that the role of the entropy factor becomes decisive: $T\Delta S_r^0(T) > \Delta H_r^0(T)$.

**Table 4.** Standard thermodynamic characteristics of the intramolecular cyclodehydration reactions of the prepolymers at a series of temperatures.[63]

| $\Delta H_r^0(T)$, kJ mol$^{-1}$ | | | $\Delta S_r^0(T)$, J mol$^{-1}$ K$^{-1}$ | | | $\Delta G_r^0(T)$, kJ mol$^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|
| 100 K | 300 K | 400 K | 100 K | 300 K | 400 K | 100 K | 300 K | 400 K |
| Group I prepolymers | | | | | | | | |
| —8.0— —140.0 | —2.5— —100.0 | 20— 100 | —60—20 | —40—70 | 170—300 | —10— —130 | —5— —100 | —10— —110 |
| Group II prepolymers | | | | | | | | |
| 10.0— 30.0 | 20.0— 40.0 | 100— 125 | —45—20 | —10—100 | 200—300 | 15—30 | 10—35 | 4.0—25 |

**Table 5.** The coefficients of the equations $\Delta G_r^0(T) = A - BT$ for the cyclodehydration reactions of the prepolymers.

| Reaction scheme | $T$, K | $A$ | $B$ | $2\sigma^*$, kJ mol$^{-1}$ |
|---|---|---|---|---|
| PAA → PI + 2H$_2$O | 300—400 | 24.0 | 0.125 | 2.5 |
| PAAA → PAI + 2H$_2$O | 300—400 | —26.0 | 0.098 | 4.0 |
| PAAA → PBBA + 2H$_2$O | 300—400 | —70.0 | 0.103 | 0.5 |
| PCBA → PADI + 2H$_2$O | 300—400 | —57.5 | 0.098 | 2.5 |
| PADI → PBTA + 2H$_2$O | 350—500 | 7.0 | 0.060 | 1.0 |
| POA → PBO + 2H$_2$O | 400—500 | 66.5 | 0.194 | 1.5 |
| PBA → PBIQ + 2H$_2$O | 400—600 | 102.0 | 0.195 | 2.5 |
| PPDA → PPDBA + 2H$_2$O | 400—550 | 97.0 | 0.201 | 0.5 |
| PATA → PTAQ + 2H$_2$O | 400—550 | 115.0 | 0.271 | 2.5 |
| PH-P → POD-P + 2H$_2$O | 400—500 | 111.5 | 0.270 | 3.0 |

*Twice the average standard error of the calculated Gibbs free energies for the cyclodehydration reaction.

$\Delta G_r^0(T) > 0$ is observed for the group II prepolymers at temperatures from 100 to 400 K, because the corresponding processes are endothermic and their positive entropies do not compensate for the enthalpy of the process: $\Delta H_r^0(T) > T\Delta S_r^0(T)$. At temperatures above 400 K, $\Delta G_r^0 < 0$ for the cyclodehydration reactions of group II prepolymers.

For the majority of the cyclodehydration reactions investigated, the standard Gibbs free energies vary linearly with temperature (Table 5), which make it possible to estimate $\Delta G_r^0(T)$ and the equilibrium constants of these processes at the temperatures used in practice for the heat treatment of the prepolymers. Such data are listed in Table 6 together with the degrees of polycondensation of polyheteroarylenes ($P_n$) calculated from the Carothers formula[65] and the degrees of conversion $X$ of the initial prepolymer into the final heterocyclochain polymer. Comparison of the data obtained with the results quoted in Table 2 shows that the cyclisation of the corresponding prepolymers in the case of PBIQ, PPDBA, POD-P, and PI at experimental temperatures went to completion, because the values of $N_2$ and $X$ are equal within the limits of the error of the calculations. The cyclisation reaction of the prepolymers associated with PTAQ, PBO, and, especially, PAI and PADI do not go to completion, because $N_2 < X$ at the experimental temperatures (Tables 2 and 6).

**Table 6.** The standard Gibbs free energies ($\Delta G_T^0$), the equilibrium constants ($Kp$), and the degrees ($X$) of the cyclodehydration reactions of the prepolymers and the degrees of polycondensation ($\bar{P}_n$) of the polyheteroarylenes formed.

| Polyheteroarylene | PAI | PADI | PI | PBO | PBIQ | PPDBA | PTAQ | POD-P |
|---|---|---|---|---|---|---|---|---|
| $T$, K | 433 | 443 | 575 | 525 | 643 | 573 | 640 | 603 |
| $-\Delta G_T^0(T)$, kJ mol$^{-1}$ | 68.5 | 101.0 | 48.0 | 35.5 | 23.5 | 18.0 | 58.5 | 51.5 |
| $K_p(T)$ | $2.0\cdot10^8$ | $8.0\cdot10^{11}$ | $2.5\cdot10^4$ | $3.5\cdot10^3$ | 81 | 44 | $6.0\cdot10^4$ | $3.0\cdot10^4$ |
| $\bar{P}_n$ | $1.5\cdot10^4$ | $9\cdot10^5$ | 152 | 59 | 10 | 8.5 | 243 | 195 |
| $X$ | 1.000 | 1.000 | 0.998 | 0.983 | 0.910 | 0.880 | 0.996 | 0.994 |

The character of the temperature variation of $X$ is significantly different for the cyclodehydration reactions of prepolymers of different groups. For the group II prepolymers (PH-P, PATA, PPDA, and PBA, Fig.5), the values of $X$ are low (0.001–0.354) in the temperature range 300 to 400 K; the degree of reaction then increases sharply with increase in temperature, reaching values virtually equal to unity (100% polyheteroarylene) at 600 K for PH-P, 650 K for PATA, 750 K for PPDA, and 850 K for PP. At these precise temperatures the equilibrium constants of the cyclodehydration reactions become equal to $5 \times 10^3$–$1 \times 10^4$.

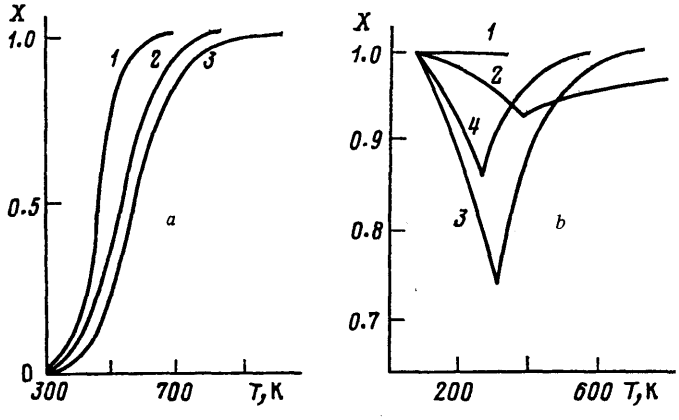



**Figure 5.** Temperature variation of the degrees of conversion $X$ in the cyclodehydration reactions: *a*) PATA (curve *1*), PPDA (curve *2*), and PBA (curve *3*); *b*) PAAA (curve *1*), PADI (curve *2*), POA (curve *3*), and PAI (curve *4*).[63]

From the thermodynamic standpoint, the preparation of fully cyclised (homounit) polyheteroarylenes from the prepolymers of the first group is possible both at low (100 to 150 K) and relatively high temperatures (500–600 K). The fact that the $N_2$ for PBO, PAI, PADI, PBBA, and PBTA do not reach limiting values determined by the equilibrium constants of the corresponding cyclodehydration reactions can be accounted for only by kinetic causes. In such cases the rigidity of the heterounit polymer formed is apparently so great that this leads to a virtual inhibition of the cyclisation process at the experimental temperature even for relatively low degrees of cyclisation ($N_2$ = 0.82 to 0.88).

## VI. CONCLUSION

It follows from the data described above that the physical state of the prepolymer is a decisive factor in the practical realisation of solid-phase cyclodehydration reactions. Namely the chemical nature of the substituents and of the atomic groups constituting the polymer chain determines the initial flexibility of the polymer macromolecules and hence the glass point of the polymer on which depends the temperature range of the cyclisation reaction. Together with this, the rigidity of the polymer increases with increasing degree of cyclisation and hence the glass point also rises. As a result, the intramolecular cyclodehydration processes hardly ever go to completion and the polyheteroarylenes formed are always heterounit polymers, i.e. contain a definite number of fragments of the corresponding initial prepolymer. In order to obtain a polyheteroarylene with a high content of cyclic fragments, the cyclisation process is therefore carried out under non-isothermal conditions.

The experimental data also show that the determination of the thermodynamic characteristics of the corresponding polymers and of their reactions constitutes an extremely effective method for the investigation of the solid phase cyclisation reactions. The study of the temperature variation of the heat capacities of the prepolymers and the final polymers and of the water vapour pressure over the prepolymers in the course of their cyclodehydration makes it possible to determine the temperature ranges in which the above reactions take place. Calorimetric study of the enthalpies of combustion of the prepolymers and the final products and of the enthalpies of cyclisation led to the development of a universal method for the determination of the degree of cyclisation of the prepolymers in intramolecular cyclodehydration processes (the method based on the calculation of the extent of the heterounit structure of polyheteroarylenes).

Analysis of the thermodynamic characteristics of the intramolecular cyclodehydration reactions makes it possible to subdivide the prepolymers into two groups differing in the character of the variation of their thermodynamic functions in the solid-phase cyclisation processes. The enthalpies of cyclisation of the group I prepolymers are negative (i.e. the reactions are exothermic) up to 373 K and positive above this temperature, the entropies of cyclisation are positive at $T$ > 100 K, and the standard Gibbs free energies are positive over the entire temperature range. The enthalpies of the cyclisation reactions of group II prepolymers are positive (the reactions are endothermic), the entropies are positive at $T$ > 100 K, and the Gibbs free energies become negative only above 400 K.

The determination of the equilibrium constants of the cyclodehydration reactions makes it possible to calculate the average degrees of polycondensation of the polyheteroarylenes at a specified temperature. These results enable

one in their turn to estimate the temperature ranges in which "defect-free" or homounit polyheteroarylenes can be obtained, which is extremely important for the development of a scientific basis for the synthesis of such polymers and for the preparation of thermostable materials from them.

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# The Applications of Chromadistillation in the Injection of Large Samples in the Gas-chromatographic Determination of Impurities

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The characteristic features of the injection of large samples into the chromatographic column with allowance for chromadistillation are considered. The theory of the chromadistillation processes occurring in the initial section of the column, which permits a rational choice of the injection parameters, is discussed and the methods and devices for the direct injection of the sample into the column are surveyed.
The bibliography includes 131 references.

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## I. INTRODUCTION

The application of chromatography for the preparative isolation of pure substances, high-temperature analysis, concentration of impurities, and various physicochemical measurements has required a continuous development of methods for the injection of large amounts of the substance to be analysed into the column. It became possible to meet these requirements with effective solution of these problems using a new version of chromatographic separation—chromadistillation (CD), developed in the USSR in recent years.[1-6] In the course of CD in a column on an inert solid filler and in a stream of carrier gas, numerous processes involving the condensation and evaporation of the components in the mixture analysed take place. Complete mixture separation is achieved either as a result of the application of a temperature field with a negative temperature gradient (thermal CD)[1,7] or as a result of preliminary injection into the column of a specified dose of a substance more volatile than any of the mixture components (limiting CD).[2,8,9] Isothermal elution (IE) of a mixture without the introduction of a limiting agent can also be included among CD processes.[10-14] The so-called "chromatography of nearly saturated vapours" (CNSV), which the present author has proposed,[15,16] occupies an intermediate position between traditional gas chromatography and CD. As in the usual chromatography, the CNSV process takes place on an adsorbent or a stationary phase (SP). However, owing to the large amount of liquid on the sorbent, the concentrations of the substances analysed in the gas phase approach the values corresponding to saturation. The limiting[9] and thermal[17] versions of CNSV have also been realised.

The development of the theory of CD methods[18,19] and the explanation of the mechanisms of the processes occurring[20-22] demonstrated their possible application for the analysis of mixtures,[23,24] continuous preparative synthesis of pure substances,[25-27] fractional distillation of mixtures of petroleum products in terms of their boiling points,[28-37] and the determination of the physicochemical characteristics of pure substances and solutions.[6,20,21,29,38-40] The characteristics of the CD process can be used to simplify the detection system[20-22,36,37,39] and also to concentrate and determine the "light" and "heavy" impurities in liquids;[33,45-50] a method has been described for the use of a CD pre-column with injection of large samples into a capillary column (CC) in the determination of impurities.[51]

A large series of studies by Grob and co-workers, who introduced the so-called "solvent effect" (SE)[52] manifested in the direct (without splitting of the stream) [splitless] injection of the sample into the column,[53-55] can be regarded as a separate special application of CD to the determination of impurities on CC. From the standpoint of classical chromatographic ideas,[56,57] a 2 μl sample exceeds the maximum permissible size for packed columns by a factor of at least 10[54] and according to estimates[56,58] the dose introduced into a CC should not be greater than $2 \times 10^{-4}$ μl. However, the sample size in studies on the SE reaches 10 μl for CC and in studies on CD using filled columns even several millilitres can be employed without impairing the efficiency of the separation. The sharp increase in the dose leads to new qualitative results. The presence of liquid components on the column (including the solvent as the main mixture component) creates conditions for the formation of narrow fronts at the boundary between the zones of the components being separated and hence for the concentration of the impurity components at these boundaries. The solvent must be regarded as the most important factor determining the efficiency of the analysis; its presence is essential for injection and it is therefore unnecessary to take steps for its removal from the system, which is usually done in the traditional injection methods.[59,60,79]

The direct injection of a large sample into the chromatographic column and also the employment of the entire initial sample (without any being discarded) in a single analytical cycle creates a new direction in the field of injection, since it makes it possible to improve the quantitative characteristics of the analysis. The amount of the component to be determined injected into the column with the sample, is then increased and the errors associated with the diversion of the stream and the fractionation of the components on evaporation are eliminated, and the probability of the thermal decomposition in the analysis of unstable compounds is reduced, since the injection is carried out at lower temperatures. With increase of the dose, the sensitivity of the

determination of the impurity component increases. In view of the great possibilities of the direct methods for the injection of the sample into CC, there has been a sharp increase in recent years of the number of publications on this field (in 1982 there were more than 100)[61] and special symposia and schools designed to learn the new injection technique have been organised.[62,63] In connection with the development of the injection methods, studies have been carried out by major investigators such as Zhukhovitskii, Grob, Schomburg and others.

The choice of the the injection system (with or without stream-splitting) depends on the specific analytical problem.[62] The direct injection methods using the SE constituted a significant step forward in the field of injection. However, the rational development of these methods was appreciably held back by the fact that the SE theory was erroneous (see below), because the processes occurring at the initial section of the column were regarded as purely chromatographic. In fact they are to a large extent of the distillation type and are covered by the new version of chromatography—chromadistillation. From our point of view, the studies on the SE can be regarded as an important application of CD for the determination of impurities in solvents. In these methods the high efficiency of the CC is combined with the possibility of greatly increasing measurement sensitivity. The fact that the development of the CD and SE processes has occurred independently in different chromatographic schools can be accounted for by the vast flood of available information which created conditions such that investigations could occur independently even in closely related fields.

The aim of the present review is to examine the entire range of problems arising in the injection of large samples into the chromatographic column. It became possible to explain all the results obtained by the SE method from the standpoint of the CD theory. Such a treatment permits a deeper understanding of the mechanisms of the processes occurring during the direct injection and indicates further ways of improving the injection technique.

## II. PRINCIPAL CONCEPTS AND TERMS

For subsequent exposition it is essential to establish a definite correspondence between the terms used in CD[5,6] and in the SE methods.[64] The processes occurring in the injection of large samples can be most rationally classified in accordance with the character of the sorption isotherms of the substances being separated. In the injection of large amounts on the SP, concave sorption isotherms are always observed (Fig. 1) and are described by the equation[65]

$$a = \frac{mp/p^0}{1 - p/p^0}, \qquad (1)$$

where $a$ is the degree of sorption, $m$ the amount of the SP, $p$ the partial pressure of the component, and $p^0$ the vapour pressure. At low relative pressures $p/p^0$ Eqn. (1) becomes identical with the linear equation for the classical gas–liquid chromatography (GLC). With increase of $p/p^0$, the non-linearity of the sorption isotherms is manifested to an increasing extent and, when $p/p^0 \to 1$, $a$ tends to infinity. Sorption isotherms of an analogous character are observed also in adsorption in capillary condensation.[66] The concave section of the sorption isotherms corresponds to the conditions in the chromatography of vapours near saturation.[15] In the absence of the SP ($m = 0$) and when pure substances are injected onto an inert layer, the sorption isotherms have the form of vertical straight lines passing through the $p = p_i^0$ points (Fig. 1). The principal version of CD corresponds to this case.[1,6,7]

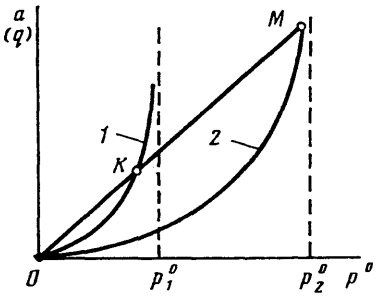



Figure 1. The sorption isotherms for components *1* and *2* at high concentrations;[9] continuous line—CNSV; dashed lines—CD; the straight line *OM* corresponds to the material balance of the components at the boundaries between the zones; $q$ is the amount of liquid per unit volume of the bed in CD.

CD processes occur in CC in two versions of the sample injection without splitting the stream (splitless injection[67]): injection with preliminary evaporation of the sample (via an evaporating injector) and with its subsequent condensation on a cooled column[53,54] or direct injection (without preliminary vaporisation) into the cooled column (direct cold on-column injection).[67] CD processes are sometimes observed even in the injection of large samples with small stream splitting coefficients (split injection).[68] The process occurring on the surface of a clean CC wetted by the liquid (flooded inlet)[69] corresponds to ideal CD.[6,7] Analysis on a SP saturated by the solvent (phase soaked)[70,71] should be included in CNSV according to the present author's ideas.[15] The isothermal process in the distribution of the sample in the form of a film (sample film)[64] corresponds to isothermal CD elution.[10–14,20,21] The preliminary deposition of the pure solvent on the layer (solvent film)[64,72,73] corresponds to the limiting versions of chromatography and CD.[8,9]

Depending on the character of the solutions of the impurity components formed with the main mixture component (solvent), different elution sequences of the impurities are observed on the chromadistogram (CDG). If the solution is ideal, the components emerge in accordance with the increase of their boiling points ($t_b$): less volatile impurities (heavy) emerge at the closing solvent front and more volatile impurities (light) emerge at the leading front.[49] In solutions with marked positive deviations from Raoult's law (with azeotropy or layer formation in the system) the elution sequence may not correspond to the $t_b$ of the components.[74] The components with $t_b$ greater than that of the solvent, which emerge at the leading front of the main component, should then be classified as light impurities. In the isothermal elution of the mixture there is a possibility of either the emergence of a less volatile impurity component after the solvent (solute lagging)[21,75] or the loss of light components simultaneously with the disappearance of the solvent zone (solute escape).[6,76] Retaining the term "solvent effect" as being more general, Grob and co-workers[77,78] introduced the concept of "solvent trapping" for all processes in which

a large sample can influence the results of sample injection, by analogy with low-temperature extraction (cold trapping). It is therefore suggested that impurities be divided into those fully retained by the solvent (trapped) and those which are only partly retained or not retained at all, which corresponds to our classification of impurities into heavy and light.[49]

Several approaches to the investigation of the impurity zone formation processes on injection of a large sample onto the column have now arisen. In studies on CD [6] the theory of processes occurring on a column with an inert filler for concentrated solutions of the components of the initial mixture has been mainly considered (on the basis of balance equations). In experiments designed to test the theory, the inlet to the column was connected directly to the detector (Fig. 2*a*), which made it possible to record the changes in the concentrations of the components in the zones formed. Additional information about the mechanism of the distribution of the liquid was provided by visual studies on the wetted section of the column. The determination of the impurities can be considered, within the framework of CD, as the limiting case where the concentrations of the components to be determined are small compared with that of the principal component. For the separate determination of the impurity components, a portion of their sample was directed to the chromatographic column after the preliminary enrichment on the CD column (Fig. 2*b*); the main bulk of the solvent was then discarded to the atmosphere.

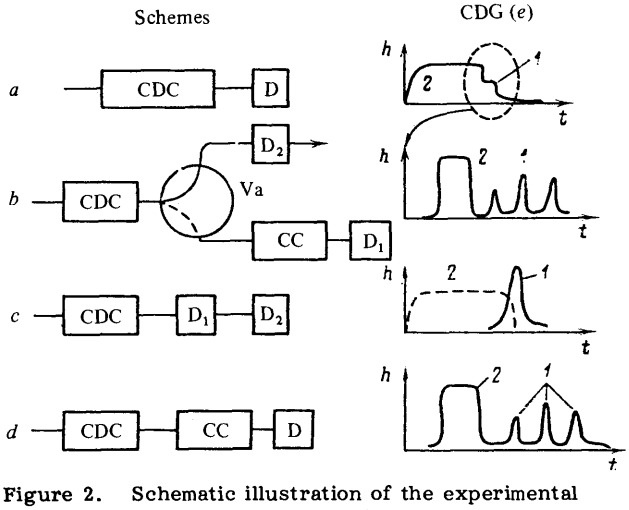



Figure 2. Schematic illustration of the experimental apparatus for the investigation of CD processes (*a*–*d*) and the corresponding elution curves (*e*); *h* = height of the signal on the recorder strip; *t* = time; CDC = chromadistillation column; CC = capillary column; Va = valve; D = detector; 1) impurity; 2) solvent.

The isolation of an impurity from the solvent has been studied both theoretically and experimentally.[72] In order to determine the location of the impurity on the elution curve, the author used an additional selective detector (Fig. 2*c*).

The approach which arose in the development of the SE is strictly experimental and involves the determination of impurities solely on CC. The samples were deposited directly in the CC and the processes occurring along its initial section could be inferred solely from the results of the separation of the components in the main section of the column containing the SP.[79] In later investigations[52,70] special attention was paid to the section for the sample distributed (in Fig. 2*d* we have specified it as the CD column) and the processes occurring along this section were studied by both visual and chromatographic (sampling) methods. The principal data were obtained as a result of detailed and laboratory experiments and the treatment was confined to the framework of development chromatography.

In the subsequent exposition we shall consider initially the theory of the process and then its experimental test and possible applications.

## III. ISOTHERMAL ELUTION OF THE MIXTURE

In isothermal elution the mixture analysed is deposited in the liquid form on an inert carrier (without SP) and is eluted from the column by a stream of carrier gas at a constant temperature. Isothermal elution (IE) is the initial stage in any of the versions of the CD separation and it is therfore essential to consider its mechanism in detail.

### 1. Theory of Isothermal Elution

Our studies in the field of CD were preceded by Kiva's investigations[10–14] on the azeotropy of solutions in which the IE of the mixture from the surface of an inert carrier was first carried out (Fig. 3*a*). The elution curve has in this instance a stepped form (Fig. 3*b*). Under IE conditions, only partial separation of the mixture takes place. The less volatile component does not emerge in a pure form until the final zone is reached. However, the result of such separation is by no means trivial. According to the theory of customary distillation,[80] when a solution evaporates from a flask, the composition of the effluent mixture must vary continuously, becoming gradually enriched in the less volatile component *1*, which is evolved in a pure form only with the last drop of the solution.

The observed picture of separation under IE conditions is determined by the occurrence of distillation processes under chromatographic conditions where a multiplicity of mixture condensation and evaporation steps are attained as the component bands move along the bed. Despite the fact that in the given case there is no sorbent familiar to workers in the field of chromatography, the processes occurring can be considered by approaching them from the standpoint of frontal-desorption chromatography,[56] i.e. in the given instance the mixture analysed is, as it were, resolved "spontaneously" as it moved along the bed. If it is supposed that the mixture components *1* and *2* have markedly different vapour pressures and that component *1* is almost involatile, then the rear edge of the zone of component *2* will migrate forwards along the column in accordance with chromatographic laws (Fig. 3*c*). On the other hand, if the less volatile component *1* has an appreciable vapour pressure, then its rear boundary will also move along the column (Fig. 3*d*). The rate of migration of the zone boundaries $u_i$ as well as the composition of the solutions formed in the zones are in general determined by the material balance equations at the zone boundaries.[6,21] This approach

is equivalent to considering the theory of the equilibrium process on the assumption that the height equivalent to the theoretical plate (HETP) is zero. In the IE of a binary mixture, the material balance equations with respect to both components at the boundary where component *2* ends yield

$$u_2 = \frac{\alpha c_2^0}{q^{II}} = \frac{\alpha c_1^0 (1 - N_1)}{q^I - q^{II} N_1}, \qquad (2)$$

where $\alpha$ is the linear flow rate, $c_i^0$ the concentrations of the saturated vapour of components *1* and *2*, $q^I$ and $q^{II}$ the amounts of liquid per unit volume of the column for bands I and II, and $N_1$ the mole fraction of component *1* in the initial mixture, Here and henceforth we shall neglect the amount of substance in the gas phase compared with the amount in the liquid phase. Having expressed $q^I$ in terms of $q^{II}$ with the aid of Eqn.(2), we obtain

$$q^I = q^{II}[\beta_{1,2} + (1 - \beta_{1,2}) N_1]. \qquad (3)$$

The equation for the rate of migration of the rear boundary of the zone of component *1* then assumes the following form:

$$u_1 = \frac{\alpha c_1^0}{q^I} = \frac{\alpha c_1^0}{q^{II}[\beta_{1,2} + (1 - \beta_{1,2}) N_1]} \qquad (4)$$

where $\beta_{1,2} = c_1^0/c_2^0$. All the principal characteristics of the IE process follow from Eqns.(2)–(4). The existence of a unique solution to the system of material balance equations shows that the zone corresponding to the mixture should be followed in the bed by the appearance of the zone of the pure less volatile component *1*. Within the limits of this zone, component *1* is present on the carrier in the liquid state and its concentration in the gas phase corresponds to the saturated vapour ($c_1^0$). According to Eqn.(3), the amount of liquid per unit volume of the column in the zone of component *1* is less than in the initial zone ($q^I < q^{II}$), since the multiplier in square brackets in Eqn.(3) is less than unity. It must be emphasised that, under the conditions of the rapid attainment of equilibrium between the vapour and the liquid, for which the equations presented are significant, the zone of component *1* is formed immediately after the introduction of the mixture. Indeed, comparison of Eqns.(2) and (4) shows that $u_1 < u_2$. For this reason, however short the time interval $\Delta t$ from the start of the experiment (provided that there is no spreading and on the assumption that the HETP is zero), a certain distance $\Delta x$ arises between the boundaries and increases as the process proceeds. This explains Fig.3*e*, which presents parts of the migration of the boundaries of the zones of components *1* and *2*.

The formation of the zone of the pure component *1* with a definite amount of liquid within the limits of the zone $q^I$ [see Eqn.(3)] and at the concentration in the gas phase corresponding to the saturated vapour ($c_1^0$) occurs as a result of repeated mixture condensation and evaporation steps. One cannot assume that the more volatile component *2* is eluted from the section where it was initially located, as usually happens in chromatography. The less volatile component *1* evaporates simultaneously. Its concentration in the vapour phase of the zone formed is higher than that in the initial zone. Component *1* condenses (dissolves) at the boundary between the zones and forms a corresponding zone I (Fig.3*d*) with a definite thickness of the liquid film. The components are separated by distillation at the boundary between the zones in such a way that the entry of one of the components into a neighbouring zone (as a result of diffusional spreading) leads to its removal as a result of the difference between the vapour pressures of the substances being separated. The opposed effects of these processes give rise to a stationary distribution of the substance between the zones whose boundary migrates in accordance with the laws governing CD equilibria.[18] By virtue of the distribution of liquid in the form of a thin layer on the packing, conditions are created which ensure the effective saturation of the gas stream by the vapours of the substances analysed. As a result, the spreading of the stationary fronts is insignificant.[19] According to the material balance equation (4), the zone of the pure component *1* should arise at the rear edge of the band. For this, it is sufficient that the two fronts of components *1* and *2* (Fig.3*d*) should traverse a distance equal to the width $\mu_2$ of the diffuse boundary (between the zones of components *1* and *2*). In the absence of equilibrium, under conditions where the HETP is not zero, the relaxation time required for the appearance of the zone of component *1* is

$$t_{rel} = \frac{\mu_2}{u_2 - u_1}. \qquad (5)$$

In non-equilibrium fractionation,[80] the attainment of a stationary distribution with formation of the zone of the pure component *1* requires that the mass-exchange and countercurrent hydrodynamic processes should go to completion throughout the volume of the sample. As in chromatography, numerous separation steps are achieved more readily in CD than in distillation.

The theory of the IE of the impurity component follows directly from the general theory of equilibrium isothermal CD[18] as a special case where the fraction of one of the components in solution tends to zero. In this case the usual CDG (Fig.3*b*) is converted into the CDG of the solvent (Fig.3*f*), at the closing front of which only a small hump due to the impurity component is observed. If the main component *2* is not registered by the detector, the observed zone of the impurity *1* should have an extended low, stepped section terminating in a narrow peak (Fig.3*g*).

We shall consider special cases of the application of Eqn.(3).

(1) When $N_1 \to 0$, the impurity is the less volatile component. The amount of liquid in the neighbouring zones is then linked by the equality $q^I = \beta_{1,2} q^{II}$. As mentioned above, in the general case $q^I < q^{II}$, since $\beta_{1,2} < 1$. This result confirms the conclusion that the zone of component *1* arises immediately (under equilibrium conditions) after the start of the IE process and that the amount of liquid within the limits of this zone should be rigorously defined and constant as a function of time (for a uniform initial distribution of the liquid).

(2) When $N_1 \to 1$, component *1* is the main one in the mixture and the impurity is more volatile than the solvent. The amount of liquid in the zones then remains virtually unchanged, i.e. $q^I = q^{II}$.

(3) When $\beta_{1,2} \cong 1$, the vapour pressures of the components are similar and the equality $q^I = q^{II}$ holds regardless of mixture composition.

(4) When $\beta_{1,2} \to 0$, the less volatile component has an extremely low vapour pressure compared with the solvent. The amount of liquid in the zone of component *1* formed then depends on its mole fraction $N_1$ in the initial mixture.

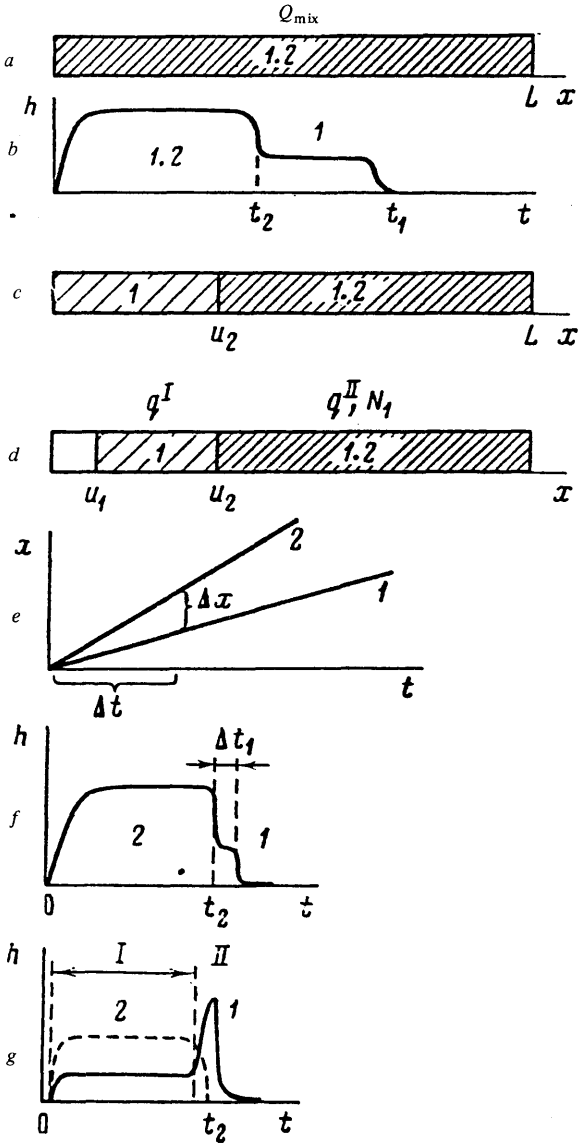



**Figure 3.** Schematic illustration of isothermal elution;[6,21] $x$ = distance along the bed; L = length of wetted section of the bed.

We shall now consider the factors which influence the impurity zone width. The width of the rear zone on the CDG (Fig.3*b*) corresponds to the less volatile component *1*. Its length ($\Delta t_1 = t_1 - t_2$) depends on the total amount of the deposited mixture ($Q_{mix}$), which wets a section of the column having a length $L$. Each boundary of the zone of component *1* crosses this section at its own rate determined by Eqns.(2) and (4). As a result, the equation for the component *1* band width on the CDG is

$$\Delta t_1 = \frac{L}{u_1} - \frac{L}{u_2} = t_2(\beta_{2,1} - 1)N_1, \qquad (6)$$

where $t_2 = Q_{mix}/v_0 c_2^0$, $\beta_{2,1} = c_2^0/c_1^0$, $Q_{mix} = q^{II}SL$, $v_0 = \alpha S$ is the volume flow rate, and $S$ the cross-sectional area of the column. It follows from Eqn.(6) that, with decrease of the fraction of component *1* in solution ($N_1 \to 0$) and as the vapour pressure of the impurity component approaches that of the solvent ($\beta_{2,1} \cong 1$), the width of the impurity zone $\Delta t_1$ diminishes. However, it must be emphasised that, under equilibrium elution conditions, component *1* is present in the liquid form within the limits of its zone, however small the latter may be, and its concentration in the gas phase corresponds to the saturated vapour ($c_1^0$). The conditions governing the formation of the pure component *1* band are defined by the relations

$$\beta_{1,2} \neq 1 \quad \text{or} \quad c_1^0 < c_2^0. \qquad (7)$$

Indeed, when $\beta_{1,2} = 1$, it follows from Eqns.(2)–(6) that $q^I = q^{II}$, $u_1 = u_2$, and $\Delta t_1 = 0$. This means that the rates of migration of the boundaries are the same and that the bands of components *1* and of the mixture of components *1* and *2* are indistinguishable in terms of the amount of liquid. When $\beta_{1,2} < 1$ and $N_1 \to 0$, the step corresponding to component *1* becomes narrow and, on spreading, it is converted into a peak on the rear solvent edge (Fig.3*g*).

Losses of the less volatile component *1* are possible in IE simultaneously with the emergence of the *1,2* solvent band (Fig.3*g*, Section 1). Knowing the rate of migration of the rear boundary of the solvent zone along the bed [Eqn.(2) for $u_2$], it is possible to obtain an expression for the retention volume at this boundary:

$$V_2 = t_2 v_0 = \frac{L}{u_2} v_0 = \frac{Lq^{II}}{\alpha c_2^0} v_0 = \frac{Q_{mix}}{c_2^0}. \qquad (8)$$

Eqn.(8) shows that the retention volume $V_2$ is independent of the way the liquid is distributed along the bed ($q^{II}$ does not enter into the final expression) and is determined by the total amount of the mixture $Q_{mix}$ introduced into the column and by the vapour pressure of the most volatile component *2*. Furthermore, regardless of the composition of the initial mixture, $V_2$ remains constant and equal to the retention volume of the pure solvent sample with a dose equal to $Q_{mix}$. This finding is associated with the fact that, when the solution is diluted, the amount and vapour pressure of the solvent in the mixture diminish to an equal extent, in proportion to its mole fraction $N_2$ in the solution.

In order to calculate the losses of the impurity component *1*, it is necessary to take into account the concentration at which it is evolved from the column during the elution period of the volume $V_2$:

$$Q_{loss,1} = V_2 c_1^0 N_1 = Q_{mix} N_1 \beta_{1,2} = Q_{init,1}\beta_{1,2}, \qquad (9)$$

where $Q_{init,1}$ is the initial content of component *1* in the initial mixture. It follows from Eqn.(9) that the fraction of component *1* lost ($Q_{loss,1}/Q_{init,1}$) is independent of mixture composition and is determined by the ratio of the concentrations of the saturated vapours of the components and the solvent ($\beta_{1,2} = c_1^0/c_2^0$). An analogous formula has been obtained in other studies.[72,76]

We shall consider an example illustrating the employment of the formulae derived. Suppose that 2 μl of hexane containing 20 p.p.m. of dodecane ($N_1 = 2 \times 10^{-5}$) has been injected into the column under normal conditions. We shall now estimate the width of the impurity zone and the losses. The amount of solvent corresponding to the dose indicated

is $2 \times 10^{-5}$ mole. For the hexane vapour pressure $p_6^0 \cong 120$ mmHg, the concentration of the saturated hexane vapour in the gas phase is $0.7 \times 10^{-2}$ mol litre$^{-1}$. If the flow rate is $v_0 = 2$ ml min$^{-1}$, then the evaporation time of the main component $t_2$ is ~$10^2$ s. With increase of the number of carbon atoms in the series of alkanes by unity, the relative volatility changes by a factor of ~3 and we therefore have for hexane and dodecane $\beta_{2,1} \cong 3^6 \cong 10^3$. Having substituted the numerical data in Eqns.(6) and (9), we find that $\Delta t_1 = 2$ s (i.e. the impurity zone is quite long) and the losses are ~0.1%.

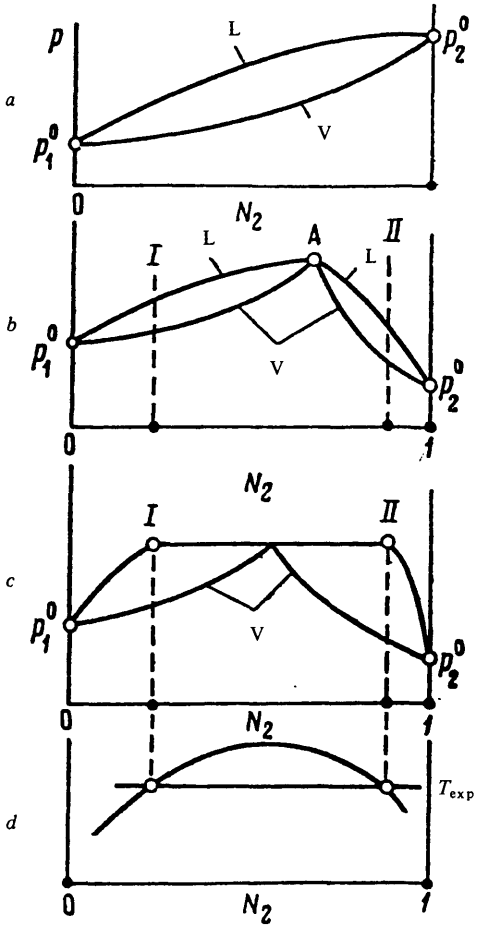



**Figure 4.** Schematic representation of the equilibrium diagrams for various systems:[80] L = liquid line; V = vapour line; *A* = point corresponding to the azeotrope: *a*) ideal solution; *b*) azeotropic mixture; *c*) heterogeneous liquid mixture (two layers); *d*) solubility curve.

We shall consider the case where the main system component (component *1*) is less volatile than the impurity (component *2*). The form of the elution curve of the impurity component and its location relative to the main mixture component will depend on the type of vapour–liquid equilibrium diagram (Fig.4). If the solution is ideal (Fig.4*a*), then, as shown in a number of studies,[10–14,74] the more volatile component *2* is evolved first and is then followed by the less volatile solvent *1* in a pure form ($p_2^0 > p_1^0$), in conformity with distillation laws. The occurrence of azeotropy or layer formation in the system (Figs.4*b*–4*d*) can alter the elution sequence of the zones on the CDG. In this case the azeotropic mixture or the solution separating into layers behaves (as in the usual distillation) as a single most volatile component. Depending on the mixture composition (I or II in Fig.4*b*) in relation to the azeotrope (points *A* in Fig.4*b*), IE can lead to the formation of the zone of one of the mixture components at the rear edge.[14,74] Thus, even if the impurity has a lower vapour pressure than the solvent ($p_2^0 < p_1^0$), there is a possibility of the evolution of the impurity component at the leading solvent edge for azeotropic and heterogeneous liquid systems.

In conformity with the above features of the IE under equilibrium conditions, the band of the volatile impurity should have a rectangular shape on the CDG. It remains to discover the amplitude and duration of this signal on the elution curve. In contrast to the heavy impurity, the concentration of the light impurity in the IE of the mixture is not higher than the concentration of the initial mixture. The concentration of component *2* in the gas phase over the solution is defined in accordance with the law governing the equilibria in real solutions:

$$c_2 = c_2^0 \gamma_2 N_2, \qquad (10)$$

where $\gamma_2$ is the activity coefficient of component *2*.

It must be emphasised that the CD analytical methods based on IE bear some similarity to the widely used vapour phase analysis,[81,82] since in both methods the components are not enriched in the gas phase. In contrast to the vapour phase analysis, in the CD methods for the direct determination of impurities[45,49] the sample injection is carried out more rationally: all the impurity is extracted from the sample and there is no need to know exactly the equilibrium parameters and hence to maintain rigorously the experimental parameters.

According to Eqns.(8) and (10), for an ideal solution the duration of the rectangular pulse of the impurity component remains constant with decrease of the concentration $N_2$ ($V_2 = \text{const.}$), while the amplitude diminishes. The activity coefficient of the impurity in a real solution can influence significantly the retention volume in the impurity band:[38,49]

$$V_2 = \frac{Q_{cm}}{c_2^0 \gamma_2}. \qquad (11)$$

As a rule, dilution of solutions with pronounced positive deviations from Raoult's law (Figs.4*b* and 4*c*) entails a sharp increase of the activity coefficient $\gamma_2$ ($\gamma_2$ may amount to tens and hundreds of units[83,84]), which may lead to an appreciable decrease of the width of the impurity component zone.

We shall quote an example of the determination of the butanol impurity in water. Suppose that the sample size is 0.1 ml ($5 \times 10^{-3}$ mole). At room temperature (25 °C), the vapour pressure of butanol is 7 mmHg, which corresponds to the gas-phase concentrations $c_2^0 = 4 \times 10^{-3}$ mol litre$^{-1}$. According to Eqn.(11), the component forming an ideal solution ($\gamma_2 = 1$) would be evolved under these conditions in a volume $V_2 = 10^3$ ml or after 50 min for a volume flow rate $v_0 = 20$ ml min$^{-1}$. Since $\gamma_2 \cong 45$ for butanol,[84] the time required to evolve the impurity is ~1 min.

We shall consider the studies on the SE mechanism in the light of the IE theory described above. In a series of communications by Pretorius and co-workers,[64,75,76,86] an attempt was made to derive an equation for the rates of migration of the solvent and sorbate boundaries and also

to determine the conditions governing the appearance of various SE regimes. A general disadvantage of the approach employed by Pretorius and co-workers,[64,75,79,85] which led to a series of incorrect conclusions, is their attempt to regard the processes in which the sorbate moves in the solvent as purely chromatographic. For example, it is impossible to set up the material balance equation at the closing solvent front immediately with respect to both components [see Eqn.(1) in Ref.85]. According to the IE theory which we described above, two cases are possible. If the impurity is lighter than the solvent, it moves ahead along the column and should not be taken into account in the material balance. For impurities heavier than the solvent, it is essential to formulate the material balance equations for both boundaries formed (Fig.3*d*). For this reason, Eqn.(6) quoted by Pretorius et al.[85] for the rate of migration at the closing edge of the solvent film can be valid only if one neglects the sorbate concentration in the gas phase.

The stages involving the formation of the sorbate film (initial and final) have been arbitrarily differentiated.[75] As mentioned above, a film of the less volatile impurity component is formed immediately (under equilibrium conditions) simultaneously with the onset of elution. Eqn.(12) obtained by Pretorius et al.[75] for the ratio of the thickness of the films in the solvent and impurity zones has narrow limits of applicability. The authors[75] assumed that the solvent, moving out of a wetted section, leaves on the surface an amount of impurity corresponding to its fraction in the initial solution. As shown above, this is possible only for $\beta_{1,2} \cong 0$ [see the special case 4 of Eqn.(3) described above]. As a result an inequality [inequality (14)[75]] was obtained, which imposes unduly rigorous requirements on the conditions for the appearance of the impurity zone:

$$\frac{p_1^0}{p_2^0} < \frac{n_1}{n_2}, \qquad (12)$$

where $p_1^0$ and $p_2^0$ are the vapour pressures of the impurity and the solvent and $n_1$ and $n_2$ are the molar concentrations of the impurity and the solvent in the initial mixture. It follows from condition (12) that the probability of the appearance of an impurity film is extremely low and it can be formed only for hydrocarbons with a molecular weight in excess of 500.[75] The CD theory presented above and the numerical example show that the impurity zone can be formed only when condition (7) is fulfilled and its formation is entirely realistic for a dodecane solution in hexane at a concentration of $2 \times 10^{-2}$ g litre$^{-1}$.

In order to compress the peaks, it has been suggested[86] that a section of CC be established in which the so-called "retention gap" is present. For this purpose, the SP is partly or fully washed out of the initial section I of the column (Fig.5). The possible mechanism of the operation of such a section has been examined: the sorbate band *1* is hardly retained and rapidly traverses section I after the solvent *2* and then, when the substance passes from the SP to the CC (Section II, Fig.5b), it is compressed. If programmed temperatures are employed, then the heavy impurity mixture components begin to be eluted from the initial section I of the column only after the attainment of the appropriate temperature.

In another communication[87] schemes designed to explain the authors' idea about the mechanism of the "retention gap" are described. In their view, the sorbent is concentrated because in section I one edge of the sorbate band (the rear edge) moves at a higher rate ($u_1'$, Fig.5c), while in the next section II, containing the SP, the other edge of the sorbate band (the leading edge) migrates at a lower rate ($u_1''$). However, this explanation of the concentration process is clearly unsatisfactory. It follows from the analysis of the operation of compound columns[56,88] that the degree of narrowing of the band is predetermined by the ratio of the rates of migration of the sorbate in the zones indicated. It must be emphasised that the concentration of the test substances in the gas phase does not change under these conditions. The sorbate band may be compressed without a change in the sorbate concentration in the gas phase on passing through the boundary at which the sorption capacity (the Henry coefficient $\Gamma_i$, Fig.5*d*) changes. Suppose that the initial width of the sorbate band is $\mu_1$ for a uniform distribution of the substance with the concentration $c_0$ in the gas phase. The rate of migration of the band along section I is $u_1' = \alpha/\Gamma_1$. The entire band passes through the boundary during the period $\tau = \mu_1/u_1' = \mu_1\Gamma_1/\alpha$. During the same period, the leading edge of the band for the same concentration in the gas phase $c_0$ traverses a distance $\mu_2 = \tau\alpha/\Gamma_2 = \mu_1\Gamma_1/\Gamma_2$ in section II at a rate $u_1'' = \alpha\Gamma_2$. If the degree of sorption in the second section is greater ($\Gamma_2 > \Gamma_1$) the band is compressed by a factor $\Gamma_2/\Gamma_1$, although the concentration of the test substance in both parts of the column remains unchanged ($c_0$).

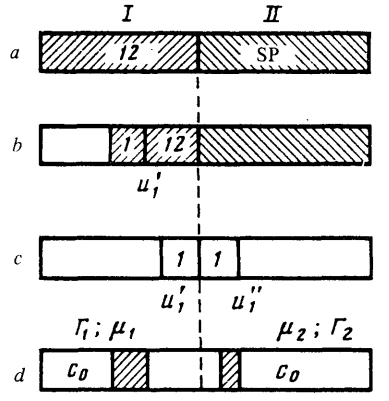



**Figure 5.** Schematic explanation of the "retention gap" mechanism;[56,86] $u$ = rate of migration of boundary; $\mu$ = width of the sorbate band; $\Gamma$ = Henry coefficient; $c_0$ = concentration of sorbate in the gas phase.

From the standpoint of the CD theory, the results described by Grob[86,87] can be readily accounted for in the following manner. The removal of the SP brings the experimental conditions closer to those of the isothermal CD on an inert carrier[6,21] (Fig.3). In the IE of the mixture on section I (Fig.3*b*), the solvent (*1*, *2*) is followed by the impurity component *1* in the liquid form. As a result of this, its concentration in the gas phase becomes a maximum and corresponds to the vapour pressure at the given temperature. Consequently, long before the rear solvent edge approaches section II with the SP (Fig.5), an increased sorbate concentration will have already appeared on section I. This increase of the concentration is in fact responsible for the narrowing of the band on the chromatogram. Furthermore, when the results of these experiments are considered, it is also essential to take into account the transition to zone

II of part of the impurity component during the elution of the mixture on section I. The final formation of the narrow peak corresponding to the entire amount of the impurity component in the sample takes place as a result of the subsequent CNSV processes (Section VI).

The explanation of the mechanism of the compression of impurities reduces, according to Grob,[52,79] to the consideration of the elution of the sorbate on a phase containing the solvent with a variable amount of liquid along the bed (Fig.6). When the sample is injected via an evaporating injector, the solvent forms, when condensed, a mixture on the SP with a constantly increasing (in the direction of motion) film thickness (zone I, Fig.6). In the first stage of the separation process, the solvent *2* moves forward relative to the sorbate 1. Next the leading edge of the migrating sorbate band in section I encounters a greater amount of the liquid phase than the closing edge. As a result of the movement at different rates of the sorbate band boundaries, the band is compressed and peaks which are narrower than in the case of split injection are formed.

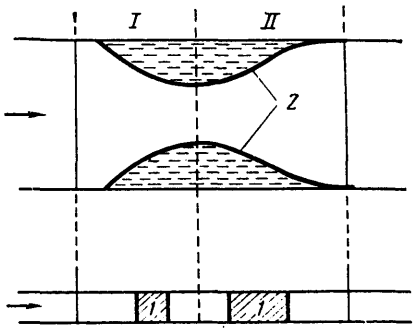



**Figure 6.** Schematic explanation of the SE mechanism in the gradient distribution of the solvent in the column:[52] 1) sorbate; 2) solvent; I) and II) direct and reverse SE zones.

The previously proposed picture of the concentration process (for section I in Fig.6) was subjected to a quantitative treatment[60,89] on the basis of the concepts adopted in GLC. It was shown that the retaining capacity of the liquid phase increases in parallel with the variation of its distribution profile. On this basis, it is concluded that the band of the impurity component on the elution curve is compressed (and the component is therefore concentrated), The correct explanation of the increase in the concentration of the impurity can be achieved on the basis of the CD theory.

The question of the concentration of the sorbate band for a longitudinal gradient of parameters (sorbability, capacity, and rate) has been frequently considered in the literature in connection with the development of versions of chromatography such as chromathermography,[56] where a moving temperature field with a negative gradient is used, and chromarheography,[90] in which a flow rate gradient is employed. It was shown in these studies that, in the absence of the flow rate gradient under the conditions of a stationary gradient of the Henry coefficient (achieved by altering the temperature or the amount of the phase), the concentration of the component cannot increase. The compression of the sorbate band does not lead to an increase in concentration, because the degree of adsorption of the component increases by a factor which is exactly the same as the factor by which the band has been compressed. Only the change in sorption capacity with time leads to an increase of concentration, as happens in chromatography with a programmed temperature[91] and in stationary chromathermography.[56] In both these versions thermal enrichment takes place, its extent being determined by the ratio of the Henry coefficients at the temperatures at which the sorbate is injected into the column and at the outlet from the latter. Furthermore, in chromathermography the "width enrichment", induced by the difference between the rates of migration at either boundary of the sorbate band, is manifested in the course of the migration of the temperature field. Grob[52,60] took no account of the capacity gradient migration factor. Only processes associated with the migration of the solvent front, the removal of the solvent by distillation, and the subsequent programming of the column temperature lead to the concentration of the impurity in the gas phase. We shall consider below the experimental data which confirmed the validity of the theoretical ideas presented above concerning the CD processes occurring in the course of IE as well as certain examples of the determination of impurities in solvents.

## 2. Distribution of the Liquid in the Column

Visual methods are important for the understanding of the mechanisms of the processes occurring in the injection of large samples. In a glass column filled with an inert carrier, which may consist of glass (etched) or metallic beads as well as diatomaceous carriers for chromatography, the section soaked with the liquid is readily seen.[21,22] A technique has been developed for the visual observation of the condensation process along the initial section of a CC.[52] The CC was first filled with a 1 *N* NaOH solution and was kept in boiling water for 4 h. As a result of leaching, the walls of the CC became appreciably clouded. It was established empirically that a thin film of the SP on the column (with a thickness $d_f = 0.12$ μm) is invisible—the column has a milky colour and is opaque. Large amounts of liquid ($d_f > 0.25$ μm) fill the pits in the column making it transparent and can be readily observed from the width of the transparent section of the column. The experiments were performed with the column thermostat at room temperature and the length and position of the ends of the soaked zone were measured after each 12 s.[52] Immediately after the injection of several microlitres of hexane through an evaporating injector, a relatively short soaked zone spread rapidly along the CC. After several seconds, the movement of the leading edge slowed down and the edge began to migrate in jerks. Within the limits of the soaked zone, waves arise and are carried forward in the form of a liquid plug which breaks up along the leading edge. After a time, the film at the closing edge became thinner and vanished. As both edges of the soaked zone move along the bed and the solvent evaporates, the leading edge slows down, whilst the rear edge accelerates until it overtakes the leading edge and the soaked zone vanishes completely.[69] The above picture of the distribution of liquid along the bed fully confirms our observations in experiments on columns filled with an inert carrier.[21] The distribution of the liquid on the surface of the filler could be assessed quantitatively from the rate of migration of the rear boundary of the soaked layer with the aid of

Eqns.(2)–(4) obtained previously. The amount of liquid $q$ retained under isothermal conditions on the carrier surface in the presence of a gas stream was calculated. This quantity amounted to 0.05 ml of liquid in 1 ml of the column for various solvents and was almost independent of the flow rate and the grain size of the carrier. An appreciable increase of $q$ at the bend in the U-shaped column is observed when the latter is positioned vertically. The constancy of $q$ enabled us[21] to develop on the basis of the theoretical equations (2) and (4) a simplified method for the analysis of a binary mixture and for the calculation of the physicochemical parameters of liquids (the vapour pressures of the components and the activity coefficients). By comparing the velocity of the soaked front and that of hexane along the SP, it was possible to estimate approximately the thickness of the solvent film in the CC, which amounted to 40 μm according to Grob's data.[52] This quantity is close to that calculated on the basis of geometrical considerations and corresponds to a fraction of liquid in the column of 0.25.

The dependence of the length of the soaked section $L$ and of its evaporation time $t_2$ on the experimental parameters has been studied.[21,69] It was found that $L$ depends only slightly on the volatility of the solvent, the carrier gas flow rate, the inlet pressure, the flow rate and method of injection of the sample, and the grain size of the carrier in the column. According to Eqn.(8), the quantity $t_2$ is proportional to the dose and decreases in inverse proportion to the volatility of the solvent.

### 3. Distribution of the Sorbate along the Bed and Determination of Heavy Impurities

When the sample is injected directly into the column, the liquid and sorbate are distributed uniformly. This can be inferred from the stepped CDG obtained when the detector is connected to the outlet from the CD column (Figs.2*a* and 2*c*). The constancy of the signal during the period of the elution of the different zones indicates the constancy of the concentrations within the limits of the zone of the distributed liquid. The application of a selective detector with respect to the impurity[72] made it possible to demonstrate this yet again. In the above study the author actually repeated Kiva's principal results[14] in the determination of impurities and, on the other hand, to some extent foresaw certain CD and SE postulates. Experiments were performed on an inert carrier (Teflon) using two detectors—a flame-ionisation detector with a high sensitivity with respect to organic substances and virtually unresponsive towards water as well as a thermal conductivity detector for water. The impurity component (Carbitol) was readily soluble in water and was less volatile. The column was maintained at a temperature below the boiling point of water. The volume of the aqueous samples was 40 μl. When the mixture was injected, the following remarkable fact, which is valid for dilute solutions, was observed. Whereas pure Carbitol in the absence of water is hardly retained in the column, when its aqueous solution is injected part of the Carbitol (*1*) is eluted together with water (zone I in Fig.3*g*), while the main bulk of the Carbitol is evolved in the form of a narrow peak (zone II) at the rear edge of water (*2*). The size of the peak formed on the "tail" of the main component is proportional to the concentration of the impurity and sample size. Deans[72] (see also his later investigation[92]) recommends that the injection of large samples into one of the columns be combined with the ejection of the main component into the atmosphere and subsequent transfer of the impurity (by means of special switching devices) to another separating column, which facilitates the operation of the latter. An example of the determination of 0.04 p.p.m. of 1,2-dimethylcyclohexane in isooctane from a 0.4 ml sample was quoted.

In our determinations of heavy impurities in organic solvents by the CD method[44,93] the sample was injected several times in succession under isothermal conditions into the column. A step associated with the impurity component (octane), whose height corresponded to its vapour pressure, was observed on the CDG after the solvent (hexane) zone. The width of the step increased in proportion to the dose, whose maximum size was about 10 ml. These experiments showed that CD makes it possible to obtain high enrichments—the concentration of the impurity increases from the initial value in solution ($N_1$) to the maximum value corresponding to the pure liquid ($N_1 = 1$) and the enrichment coefficient is $10^3$–$10^4$. In the development of an indirect CD method[45] for the determination of impurities in water (with preliminary extraction of the sample by a volatile solvent and its subsequent CD analysis) the losses of the impurity component arising in isothermal analysis [see Eqn.(8)] were taken into account in constructing a linear calibration.[93]

Whereas on filled columns the solvent and the sorbate are as a rule distributed uniformly, on CC, in particular when the sample is injected through an evaporating injector, certain characteristic features are observed. The use of a solvent during the concentration of the sorbate induces in many instances a distortion of the peaks—they are greatly broadened and even split into two components on the chromatogram. The distribution of the sorbate within the limits of the soaked section of the CC has been investigated using the method described by Grob.[69] The distribution of perylene on the surface of the CC after the introduction of concentrated perylene solutions was investigated in ultraviolet light (in a separate chamber). Subsequent experiments with dilute perylene solutions were performed under the same injection conditions with recording of the chromatogram and were compared with visual observations. When the sample is injected directly into the CC at 25 °C, the impurity is not always distributed on the column in the form of a uniform film. Depending on the conditions, most of the impurity component is concentrated at the ends of the liquid zone with a length amounting to several centimetres. In this case split peaks are observed on the chromatogram, the first of which is usually higher than the second. When perylene is injected through an evaporating injector, it is concentrated mainly in the hot zone at the inlet to the CC. The peaks then have the form of a "stool" with the flat portion turned towards the start of the experiment. The distorted peaks of all the components were clearly seen in experiments on a mixture of $C_{12}$–$C_{36}$ n-alkanes diluted with acetone ($1 : 2 \times 10^5$) in which the temperature was programmed in the range from 30° to 300 °C.

The conditions governing the formation of a narrow band of impurities when the sample was injected into the CC through an evaporating injector have been investigated.[79] The evaporator and column temperatures during the injection period are kept constant (25 °C). Ten solvents of different classes with $t_b$ up to 69 °C were investigated. In order to improve separation, the author recommends that the column temperature be reduced, that a less volatile solvent be chosen for the analysis of heavier alkanes, that a fairly large amount of liquid be deposited, etc.

The main principles governing the broadening of the bands on the bed in CC and the distortion of the peaks on the elution curve have been formulated.[86] It has been shown in relation to the analysis of the $C_{22}$, $C_{26}$, and $C_{30}$ n-alkanes that repeated decrease of the thickness of the SP film (by washing it off) in the range from 2 to 0.03 μm leads to a proportional decrease of the peaks. In fact the author proceeded to the examination of CD on an inert carrier in this instance.

Experience gained in the application of the SE showed that the injection of large doses in CC washes the SP out of the initial section of the column, leads to its accumulation at some distance from the point of injection, and finally results in the impairment of the efficiency of the column and even in its blocking. In order to eliminate these undesirable phenomena, a method has been developed in which the SP is washed out of the first two metres of the CC in a preliminary step.[94] For this purpose, approximately 150 μl of methylene chloride, containing 0.1% of Carbowax 1000, was introduced from a microsyringe via an elastic connection, and then, after several seconds, the liquid was blown out in the opposite direction. The operation was repeated three times. Along the section of the CC 2 m long, it is possible to deposit 5–8 μl samples. Various procedures for the preparation of CC without SP along the initial section, in which the SP is extracted or burnt off, have been described in detail.[87] Empty pre-columns connected to the CC either by a flexible Teflon tube or via screw thread or glued junctions have also been used. The MEGA Company supplies prepared CC with an empty end section (3 m long).

A series of new factors leading to the broadening and distortion of the peaks have been treated systematically[77,78,95] and the mechanism of the formation of the sorbate band as a function of the experimental conditions has been considered. The only injection method ensuring sharp initial sorbate bands involves split injection. The remaining methods require a concentration process over a period up to at least 0.1 s (or over several mm along the bed). The broadening of the bands in the injection of large samples can arise for two reasons. Firstly, when samples are injected through an evaporating splitless injector, the process in which the sample is transferred from the evaporator to the CC bed entails an appreciable increase in the injection time (on average up to 30–60 s), which induces the spreading of the peaks on the chromatogram—the so-called "band broadening in time". The peaks of the components on the chromatogram have the same width. The broadening of the peaks is eliminated by improving the condensation conditions, by employing an additional solvent (limiter) (see Section IV), and by programming the CC temperature (the broadening of the peaks is not observed for substances which are eluted at a column temperature 60–80 °C higher than the initial temperature). The second cause of the broadening of the band is associated with the distribution of the liquid and together with it also of the sorbate over a definite fairly long section of the CC—the so-called "band broadening in space". On average, the soaked section can occupy between 10 and 60 cm of the length at the inlet to the CC. In this case the magnitude of the effect depends on the ratio of the lengths of the wetted and SP-coated sections of the column. Thus approximately 2% of the length of a 15 m column is wetted, which decreases the number of theoretical plates (NTP) by a factor of ~5. The "band broadening in space" is manifested for peaks of heavy components (with a relative capacity $k' > 30–50$) and is independent of the programming of the temperature. It has been noted[77,78] that all the types of spreading indicated above depend on the ratio of the vapour pressures of the substance analysed and the solvent. The processes on the solvent are regarded as the first stage of the chromatographic separation. In order to investigate the process involving the isolation of the impurity from the solvent, a method has been developed for sampling at different stages of the distillation of the solvent.[78] A capillary section 1 m long, deactivated with Carbowax, was placed between the injector and the CC. This pre-column, containing the entire sample, was maintained for a definite period at the inlet of the CC and then the residue from the sample was blown out into the atmosphere and the experiment was terminated. When a non-polar solvent (hexane) was used, the higher-boiling alkanes always emerged in the form of narrow peaks and were eluted from the pre-column attached to the CC together with the last portion of the solvent. If the experiment was performed under conditions where there was no condensation (using pentane as the solvent injected via an evaporator), then all the peaks were broadened to the same extent, corresponding to the time taken to transfer the sorbate onto the CC. The formation of narrow alkane peaks can be accounted for by the occurrence of two types of CD processes. In the first place, less volatile impurities, having a much lower vapour pressure than the solvent, are concentrated near the rear solvent edge along a short section between the evaporator on the CC. Furthermore, as a result of limiting CNSV processes (see below), the possibility of the appearance of steps before the peaks is eliminated. The influence of these two CD processes on the formation of narrow peaks was not considered by Grob.[77,78]

### 4. Distribution of the Sorbate along the Bed and Determination of Light Impurities

In the development of a direct method for the analysis of organic impurities in water, it was established that all hydrocarbons sparingly soluble in water emerge from an isothermal CD column almost at once in a single peak.[45,46] The possibility of evolving the impurity in the form of a narrow zone, enabled the authors to develop a series of CD methods for the determination of petroleum products in water.[49] The possibility of determining the solubility of $C_6$–$C_9$ alkanes in water at concentrations of 1–10 mg litre$^{-1}$ and also of determining the content of petrol fraction hydrocarbons in water has been demonstrated.

In the determination of light impurities on CC, their evolution with the first portions of the solvent was also observed.[78] Thus approximately 90% of 2-propanol was transferred from hexane to the CC over a period of 20 s. As a rule, such conditions arose when there was a marked difference between the polarities of the solvent and the sorbate (for example, for ethanol as the impurity, hexane as the solvent).

Together with the normal SE, the "reverse solvent effect", manifested by the broadening and distortion of the peaks due to substances emerging before the main component, has also been discussed.[96] Both light impurities ($C_7$–$C_{10}$ n-alkanes and certain aromatic compounds) and heavy impurities (durene and dodecane) have been determined in solution in undecane. The experiments were performed with slight stream splitting (1:100) for a dose of 0.015–8.0 μl. The efficiency, expressed in terms of the number of theoretical plates, fell with increase of the dose by a factor of 2–4 for the light components. The explanation is that the sorbate band falls within a field with a negative liquid phase distribution gradient (section II, Fig.6). As a result of the arrest of the rear edge of the band and the acceleration of the leading edge, a reverse SE, leading to the distortion

of the peaks, is manifested. For the heavy component (durene), an increase of the NTP by a factor of 9 was observed.[96] This effect has also been discussed by Yang et al.[97] and Brötell et al.,[98] who obtained anomalously high efficiencies with respect to $C_8$ and $C_{10}$ n-alkanes (4390 and 14400 plates $m^{-1}$ respectively). The formal application of the familiar expression for the NTP (Fig.7).

$$n = \frac{5.54}{L}\left(\frac{t_R}{\mu}\right)^2$$

leads to unduly high values of this quantity. In the determination of the true retention times of the components for the correct calculation of the thermodynamic characteristics of the substances and their identification, it is essential also to take into account the shift of the retention times. The use of a heavier solvent results in an increase of the elution time of the impurity components. This effect is attained on a lighter solvent (pentane, hexane) with increase of the dose.

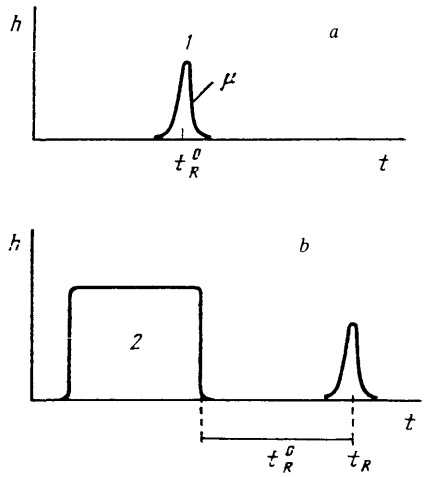



Figure 7. Schematic explanation of the calculation of the NTP ($n$) in the injection of a sample without solvent ($a$) and with solvent ($b$): 1) impurity; 2) solvent; $t_R$ = retention time; $\mu$ = peak width.[96]

Factors leading to the distortion of the peaks have been examined in relation to the determination of chloroform impurities in solvents.[99] The authors claim that the distortion of the peak owing to the partial trapping of the impurity cannot be eliminated with the aid of the subsequent process on the solvent-saturated SP. Chloroform peaks with ideal shape were obtained only when water, acetone, and diethyl ether were used as solvents combined with a polar SP. In the first two cases the successful result can be accounted for by the formation of azeotropes in the systems indicated, which lead (as mentioned above) to the rapid separation of the impurity from the main component.

Studies have been made[100,101] on the additional spreading of the peaks due to substances emerging before the solvent. In experiments with model mixtures of $C_5$–$C_{12}$ n-alkanes in octane and ethanol, it has been shown that "effectively" trapped components emerge in narrow peaks and "poorly" trapped components emerge in the form of broad steps. It is noteworthy that the boundary between the "poorly" and "effectively" trapped impurities is indefinite and is associated, according to the authors,[100] with distillation processes. In conformity with the classification of impurities into light and heavy presented above,[49] one must distinguish impurities capable of forming solutions having a vapour pressure greater or smaller than that of the solvent. Thus when ethanol is used as the main component, all the alkanes up to n-heptane form azeotropic mixtures[83] and are evolved at the leading edge of the solvent. Higher-boiling n-alkanes, which do not form azeotropes, should emerge after the more volatile solvent. The recommended increase of the initial column temperature in order to reduce the solvent injection time can lead only to a partial narrowing of the peaks.[100] A more radical means of compressing the peaks of light impurities involves the creation of a negative temperature gradient (see Section V).

The questions examined in this Section show that isothermal elution constitutes the initial stage of the CD separation and in many instances can be used directly to concentrate and determine impurities.

## IV. LIMITING CHROMADISTILLATION

In the previous Section it was shown that the IE of a mixture entails extensive spreading of the peaks of both light and heavy impurity components. The broadening of the sorbate bands as well as the losses of substances associated with the evolution of the impurity component together with the solvent zone can be eliminated with the aid of limiting CD.[2,8,9]

Limiting CD consists in a procedure where a dose of the pure substance, whose vapour pressure is greater than or equal to the vapour pressures of the mixture components is deposited beforehand, before the injection of the mixture to be separated in a column filled with an inert carrier. The main mixture component (the solvent) can be used as a compound of this kind, referred to as the limiter, when the determination of the lighter components is not required.

The mechanism of the action of the limiter on a column without a SP is explained in Fig.8. In the initial instant the limiter *3* is deposited on section II of the column and the mixture (*1*, *2*) is deposited on section I (Fig.8*a*). In the first elution stage (Fig.8*b*), the following processes take place. The frontal IE of the mixture, described previously (Fig.3) and leading to the evolution of the pure less volatile component *1*, takes place at the rear edge. At the leading edge of the *1*, *2* zone the saturated vapour is transferred by the stream of carrier gas to section II and is condensed at the rear edge of the limiter. In conformity with distillation laws,[80] the formation of the zone comprising the mixture having the initial composition should be accompanied by the simultaneous liberation of the pure more volatile component *2*, which forms its own zone intermediate between the zones of the mixture and the solvent. It follows from the theory of limiting CD[21] that the rate of migration of the rear edge of the mixture zone ($u'_2$) (Fig.8*c*) is greater than the rate of migration of the leading edge ($u''_2$):

$$u'_2 = \frac{\alpha c_2^0}{q_{1,2}} > u''_2 = \frac{\alpha c_1^0}{q_{1,2}}, \qquad (13)$$

where $q_{1,2} = q^{II}/(N_2 + \beta_{2,1}N_1)$ is the amount of the liquid mixture *1*, *2* per unit volume of the column on section II, as a result of which the zone of the *1*, *2* mixture on the bed disappears and ultimately the mixture components are fully

separated (Fig. 8*d*). A typical CDG for this case is illustrated in Fig. 8*e*. Thus the separation in limiting CD is a result of numerous frontal separation processes at the rear and leading edges of the liquid. A relation has been derived[6,8] between the amount of limiter $Q_{lim}$ and the dose $Q_{mix}$ (of a mixture of known composition) which ensures complete mixture separation:

$$\frac{Q_{lim}}{Q_{mix}} > \frac{N_2 + \beta_{2,1} N_1}{\beta_{2,3}(\beta_{2,1} - 1)}, \qquad (14)$$

where $\beta_{2,1} = c_2^0/c_1^0$ and $\beta_{2,3} = c_2^0/c_3^0$. It follows from this relation that a definite length of the bed is required along which the rear boundary of the *1*, *2* zone formed (Fig. 3c) should be able to catch up with the leading boundary before it emerges from the column. In essence the main mixture separation process takes place and is completed on section II of the limiter. Special cases for two problems in the determination of impurities follow from Eqn. (14).

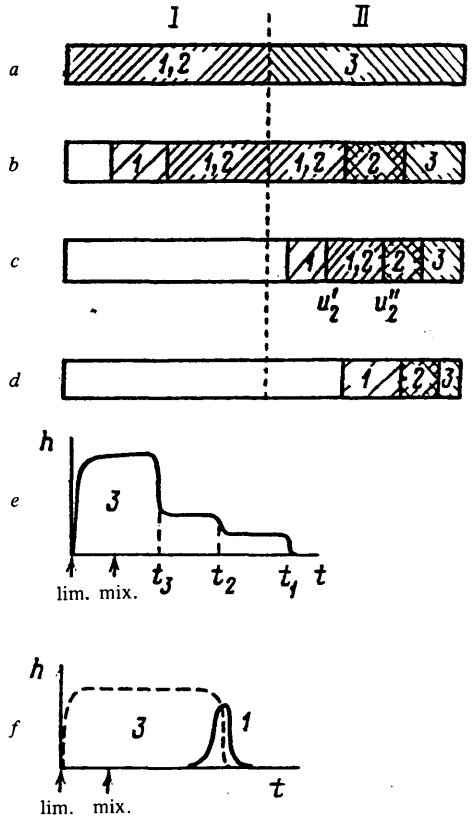



**Figure 8.** Schematic illustration of limiting CD.[21]

$N_1 \to 0$—determination of a heavy impurity. For this purpose it is useful to employ the pure solvent as the limiter. Then $\beta_{2,3} = 1$ and we obtain the relation

$$Q_{lim} \geqslant Q_{mix}(\beta_{2,1} - 1). \qquad (15)$$

In contrast to the CDG of the impurity component obtained in IE (Fig. 3*g*), in this case a narrow peak of the impurity (without a low-slope stepped section) is observed on the elution curve and is located at the rear edge of the solvent (Fig. 8*f*).

$N_1 \to 1$—determination of a light impurity. Under these conditions, Eqn. (14) assumes the form

$$Q_{lim} \geqslant Q_{mix}\beta_{3,1}/(\beta_{2,1} - 1). \qquad (16)$$

The impurity will be concentrated at the boundary between the limiter and the main mixture component.

It follows from Eqn. (14) and its corollaries that in most practical cases ($\beta_{2,1} < 2$) the complete separation of the mixture and the removal of the impurity require that the volume of the limiter should as a rule exceed the dose of the mixture to be separated. Large amounts of the limiter are required both in the separation of the mixture components with similar vapour pressures and in the isolation of the more volatile mixture component and when a more volatile limiter is employed.

Questions concerning the theory of the impurity isolation process, which in fact constitutes limiting CD, have also been examined by Pretorius et al.[76] A relation was obtained for the solvent and sample doses which ensure the complete isolation of the heavy impurity component in the form of a single peak on the chromatogram. It is identical with our Eqn. (15). The derivation was based on the consideration of the elution of the impurity component zone in terms of the more volatile solvent. The authors determined the rate of migration of the leading edge $u_2''$ in accordance with the partition coefficient, which is in the general case incorrect because, it follows from Eqn. (13), that at high sorbate concentrations the rate $u_2''$ depends on the mixture composition.

We carried out an experimental test of the principal relations of limiting CD on a packed column[6,8] and showed that the use of the limiter leads to the concentration of the substances. Thus, if the concentration of the test substance in the gas phase is less than the vapour pressure and the substance enters the column filled with the more volatile solvent together with the stream, then the given component will accumulate at the rear edge of the solvent and, as a result of the CD separation, can form a zone of the pure liquid at the concentration of the saturated vapour in the gas phase. This accumulation principle has been realised[43,44] in the determination of heavy impurities in a solvent and it has been shown that, after a single injection of the limiter dose, it is possible to inject repeatedly the mixture doses and obtain a proportional accumulation of the impurities.

Analysis of light impurities in solvents, even when the impurity components are sparingly soluble, is frequently hindered by the slowness of their evolution. Thus, in the direct analysis of alcohols in water, the impurity zone emerges from the preliminary CD column in the course of several minutes in the form of a peak with an extended "tail". The introduction of the limiter (ethanol) makes it possible to collect the entire test substance in the form of a narrow step at the closing front of the limiter. In studies [48,51] on the analysis of impurities as fermentation products (wine-making materials, brandies, etc.), it was noted that the accumulation of impurities at the boundary between two solvent zones (ethanol–water) leads to additional compression of the impurity peaks. A method was developed for the determination of impurities in wine-making materials, which are evolved at the leading front of ethanol, at the boundary between ethanol and water and at the rear edge of water.[48]

In studies by non-Soviet workers, the principle of limiting CD has been used to determine impurities using direct injection.[72,73]

The preliminary injection of the solvent to ensure the complete isolation of the impurity was first used by Deans.[72] Thus, in order to determine Carbitol to an aqueous 20 μl sample, 20 μl of pure water was introduced into the column beforehand. The author points out in this connection the necessity to select the appropriate solvent dose in order to attain the complete isolation of the impurity component.

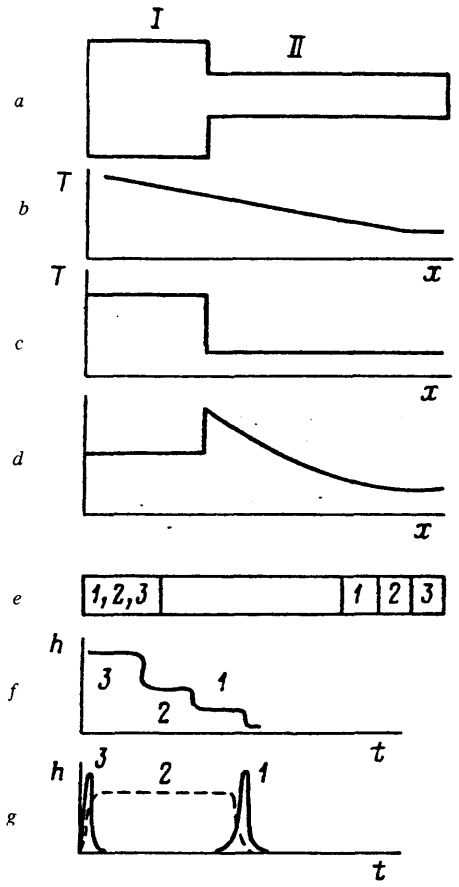



**Figure 9.** Schematic illustration of thermal CD:[7] *a*) junction between the injector (I) and the column (II); *b*) temperature field in thermal CD; *c*) ditto with evaporating injector; *d*) ditto along CD column; *e*) distribution of components I, II, and III along the bed; *f*) CDG of the mixture; *g*) CDG of impurities *1* and *3* in the solvent *2*.

A method for the injection of large gaseous samples (in vapour phase analysis), which is a development of the direct injection method with SE, has been considered.[73] Samples of mixtures of octane and air were injected by means of the usual injector, permitting the splitting of the stream. These experiments must be regarded as the version of limiting CD in which the condensation of large gaseous samples in the CC is achieved with the aid of the preliminary introduction of the solvent into the column. The unduly low heights of the octane peaks observed in experiments following an increase of the interval between the injection of the liquid and gaseous samples are due to the fact that the main bulk of octane failed to "catch up" with the rear edge of the limiter (Fig. 8c). The conditions under which the SE is manifested were investigated quantitatively in the above study. The simultaneous injection of the solvent and the gaseous sample naturally led to a negative result—the bulk of the octane passed through the CC without being retained on hexane. After the replacement of the solvent by pentane and the increase of the dose from 2.5 to 3.5 μl, the limiting effect was not observed at a CC temperature of 35 °C (apparently pentane did not condense). At room temperature a moderate impurity retention effect was noted.

The limiting CD process examined in this Section constitutes an effective means for isothermal concentration and isolation of impurities from solvents.

## V. THERMAL CHROMADISTILLATION

As already mentioned above, the IE of a mixture involves only partial separation into individual components (Fig. 3). In order to achieve complete separation of the mixture, it is necessary to ensure conditions for the condensation of the saturated vapours formed at the leading edge of the band. The simplest method whereby condensation conditions can be created involves the use of a temperature field with a negative gradient (the temperature should decrease monotonically from the inlet to the outlet from the column—Fig. 9*a* and 9*b*). Under the conditions of thermal CD,[7] the repetition of the condensation and evaporation processes is achieved as a result of the movement of the entire mixture along the bed, which leads to its separation into the pure substances at the outlet from the column (Fig. 9*e*). The elution curve (the CDG) has a stepped form (Fig. 9*f*), where the height of the step corresponds to the vapour pressure and its length to the amount of each component. In CD the impurities are concentrated at the leading or rear edge of the main component (depending on the type of solution formed).[49] As a rule, the concentration of the impurity substance in the sample is insufficient to form a separate zone and for this reason the impurities are isolated in the form of narrow bands (Fig. 9*g*).

The temperature gradient is the most effective means of separation in CD. In contrast to chromatography, a stationary temperature field in CD results in the concentration of the substances, since repeated mixture condensation steps take place continuously along the bed, each leading to the liberation, in conformity with distillation laws,[80] of the lighter component and to the separation of the mixture as a whole. It is noteworthy that a longitudinal temperature gradient also arises in fractionation, but its character is wholly determined by the composition of the mixtures formed in each section of the column. In the continuous separation of a mixture under adiabatic conditions, a stationary distribution of concentrations arises along the packing. The heat supplied to the lower part of the column leads to the boiling of the liquid in all the sections; the temperature can then vary only in the range of the $t_b$ of the components to be separated. In contrast to fractionation, the temperature gradient in CD is specified from outside. The process is based neither on boiling nor on evaporation. The discrete nature of the injection, the absence of a countercurrent flow, and movement along the bed, as in chromatography, lead to a simpler way of achieving multiple separation steps, which

makes it possible to increase the efficiency of the separation. In contrast to chromatography, under conditions where components are separated by thermal CD (Fig. 9e) stationary fronts are observed[19] and there is no progressive spreading of the bands. In thermal CD the separation proceeds not only via frontal stages at the rear and leading liquid edges (as in limiting CD) but also along the entire layer of the mixture, since condensation takes place in all the sections of the column. Visual studies of thermal CD have shown that each component of a mixture boiling over a wide range occupies a definite section of the column within the limits of which a uniform distribution of the liquid on the bed is maintained ($q$ = 0.2 ml of the liquid in 1 $cm^3$ of the column). Both boundaries of a strongly wetted section (leading and rear) migrate along the bed in such a way that the zone width remains unchanged. This made it possible to develop a simple visual method for the analysis of high-boiling substances.[22]

In contrast to IE (section III) and vapour phase analysis,[81,82] thermal CD leads to the concentration of light impurities. Thus it has been shown[50] that, in the analysis of a butanol–water mixture on an isothermal column, butanol emerges in the form of a peak with a highly extended base despite the presence of positive deviations from Raoult's law ($\gamma_2$ = 45). The creation of a longitudinal temperature gradient compresses the alcohol band and enriches it by a factor of 250. As mentioned above, in effective thermal CD, the impurities are evolved at both edges of the principal component. There is therefore a possibility of different versions of the group separation of impurities. In relation to the isolation of butanol and acetic acid from water, it has been shown[15] that, by varying the dose, it is possible to regulate the distance between the components indicated.

All the principal results in the analysis of impurities have been obtained under the conditions of thermal CD. The methods described were developed mainly for the determination of impurities in aqueous systems.[49] Two versions of analysis are proposed: the direct version where the aqueous mixture to be analysed is injected directly into the CD column and the indirect version where the substances to be determined are first extracted with a solvent. The degree of the additional enrichment as a result of extraction was (depending on the ratio of the volumes of the aqueous sample and the solvent) between 40 and 200. On the basis of the first version of analysis, the following procedures have been developed:[45,51] determination of hydrocarbons dissolved in water, isolation of the petrol fraction and its separation by group distillation, the determination of light alcohols ($C_1$–$C_5$) which are readily soluble in water, and the separate determination of the sparingly soluble fractions of high-boiling alcohols ($C_7$–$C_{13}$). A method for the determination of impurities, which are evolved before ethanol, at the ethanol–water boundary, and after water, has been developed for the analysis of fermentation products containing two main components (water and ethanol). The relative standard deviation in the determination of alcohols at the level of 10–100 mg $litre^{-1}$ was 0.2–0.5 for a fiducial probability of 0.95. When measurements were made at the level of the limiting permissible concentrations (LPC) of alcohols in drinking water (0.1 mg $litre^{-1}$), a 20–30% change in the composition of the solutions was observed after several hours. The use of a solvent in the indirect methods (hexane or carbon tetrachloride) as well as an additional solvent in the direct methods (ethanol) permits the determination of components which are sparingly soluble in water and which form emulsions with the latter. The sensitivity of the indirect analytical methods for the petroleum products with $t_b$ corresponding to the $C_7$–$C_{20}$ n-alkanes was 0.014 mg $litre^{-1}$ and was limited by the purity of the solvents employed.[45,93]

The characteristics of CD, which arise when a moving temperature field with a negative gradient is employed—the so-called chromathermodistillation (an analogue of chromathermography), have been considered.[15,105,106] This method ensures the concentration of impurities less volatile than the solvent as a result of their evolution at higher temperatures and also makes it possible to shorten the duration of the analysis.

We shall now consider studies in which the SE was ensured by a negative temperature gradient along the column. In the initial version of the direct injection method,[53,55] the usual injectors were employed for the CC in which the outlet for discarding the carrier gas was closed during the injection period (30 s). A sharp temperature gradient was then employed (Fig. 9c)—the sample was evaporated at a high temperature (210 °C) and was condensed on the CC at room temperature. In the first studies the compression of the impurity band was observed. In order to investigate the compression effect, the sample was injected over different periods ($\tau_{inj}$) and the width of the sorbate band on the elution curve ($\tau_{el}$) was measured. The ratio of these quantities characterised the degree of enrichment, which gradually increased in the series of cycloalkanes from $C_4$ to $C_8$ and amounted to ~10. A method was also developed for analysis in which the solvent is discarded. A section of a capillary 1.6 m long was connected to the injector, the working flow rate was established, the sample was injected into the evaporator (at 210 °C), and it was condensed on the capillary at 25 °C over a period of 30 s. The gas flow was then stopped, the outlet end of the capillary was connected by means of a Teflon tube to the main CC, and the experiment with programmed temperature was begun. It was then shown that the losses of light components ($C_4$–$C_5$), emerging after the solvent, are 60–80% and those of the heavy $C_6$ component are 10%. The experiments in which the inlet capillary was cut into three sections (40, 40, and 80 cm) and the contents of the latter were subsequently analysed on the CC confirmed that volatile impurity components accumulate at the closing solvent front in CD. The use of an unduly short (albeit with a high gradient) temperature field (Fig. 9c) for a small difference between the vapour pressures of the solvent and the substances analysed leads to a decrease of the efficiency of the CD separation. The incomplete extraction from the solvent of even heavy impurities shows that a single condensation step in the thermal version of CD is insufficient.

It has been noted[79] that the difference between the temperatures of the evaporator and the CC can be used both in the vapour phase analysis in the absence of a solvent and in the analysis of a sample with a solvent. When the column is moved in the thermostat, a large gradient is established which improves the shape of the peaks.[86]

It was not clear from previous studies of the SE to what extent this effect determines the impurity concentration process, because one could also postulate that it is associated with the low-temperature extraction. The conditions making it possible to differentiate these processes have been investigated[94] using an injector, for the direct injection of the sample into the CC.[67]

Certain theoretical questions associated with the distortion of the sorbate band in direct injection into a cooled column have been examined.[102] The authors assumed that direct injection leads mainly to a distribution of the liquid with decreasing amount of the latter along the carrier gas stream. For this reason, one should have observed a distortion due to the reverse SE (Fig. 6, section II).[96] When the initial

section of the CC is unduly cooled, a temperature gradient, increasing along the CC, arises, which also enhances the "reverse SE". It follows from the examination of the retention characteristics adopted in GLC[89] that this entails the broadening of the band in the temperature field. The authors[102] suggest that the peaks be compressed by establishing a negative temperature gradient, i.e. in essence by intoducing the elements of thermal CD into the experimental technique. For this purpose, in the devices described by Galli and co-workers[103,104] it is necessary to supply cooling air in the direction opposite to the flow of the carrier gas from the side of the warmer column thermostat.

In order to assess the possibilities of the proposed method and also for comparison of the expected results with the data actually obtained we shall carry out the following calculation. We shall assume that the concentration of the impurity substance is measured by a flame-ionisation detector whose sensitivity is the same in all the methods compared and amounts to $c_{fid} \cong 10^{-4}$ (vol.%). With the aid of a linear detector, such a concentration can be recorded on the $10^{-11}$–$10^{-12}$ A electrometer scales. The minimum concentration which can be determined in the initial mixture (injected into the chromatograph) is related to the experimental parameters by the following formula:

$$c_{min} = \frac{c_{fid} v_0 t_\mu M}{2.24 V_{ds}} \text{ (mg litre}^{-1}\text{)},$$

where $v_0$ is the carrier gas flow rate (ml min$^{-1}$), $t_\mu$ the peak width on the chromatogram (min), $M$ the molecular weight of the substance analysed, assumed to be 100, and $V_{ds}$ the volume of the sample injected (ml). We shall examine the numerical data for two principal cases.

1. Analysis on a filled chromatographic column with injection of the sample into the CD pre-column. We shall assume that $v_0 = 20$ ml min$^{-1}$, $t_\mu = 0.5$ min, and $V_{ds} = 1$ ml. In this case $c_{min} = 5 \times 10^{-2}$ mg litre$^{-1}$, while the concentration actually determined[45] was $5 \times 10^{-3}$ mg litre$^{-1}$.

2. Analysis on a CC using the direct sample injection methods. If $v_0 = 2$ ml min$^{-1}$, $t_\mu = 2$ s, and $V_{ds} = 10$ µl, then $c_{min} = 3 \times 10^{-2}$ mg litre$^{-1}$. The results of the analysis of solutions containing 1–20 p.p.m. of the test substance have been quoted in studies on the SE. In both cases presented here, $c_{min}$ is of the same order of magnitude despite the difference in the dose by a factor of 100. This can be explained by the higher efficiency of the CC, working at a lower flow rate, which leads to the isolation of the impurity in a small volume and hence to a greater sensitivity of the measurements on the CC. It follows from the data presented that the use of the CD pre-column in combination with a CC can increase the sensitivity by a further two orders of magnitude, whilst retaining the efficiency of the CC, which makes it possible to attain a level of measurable concentrations of about 0.1 p.p.m.

Studies on thermal CD have shown that the temperature gradient influences the mixture separation to the greatest extent. In order to enhance the concentrating effect, one can combine the limiting and thermal CD processes.[74]

## VI. CHROMATOGRAPHY OF NEARLY SATURATED VAPOURS

This Section deals with studies in which the stationary phase is greatly overloaded by the solvent during the sample injection period. The isolation of the impurity components along the initial section of the column is accompanied by the interactions of the sorbates not only with the SP and the solvent but in many cases also with one another. These phenomena are described by the chromatography of nearly saturated vapours[9,15,17] in which one considers processes at high concentrations corresponding to the concave sections of the sorption isotherms (Fig.10*a*).

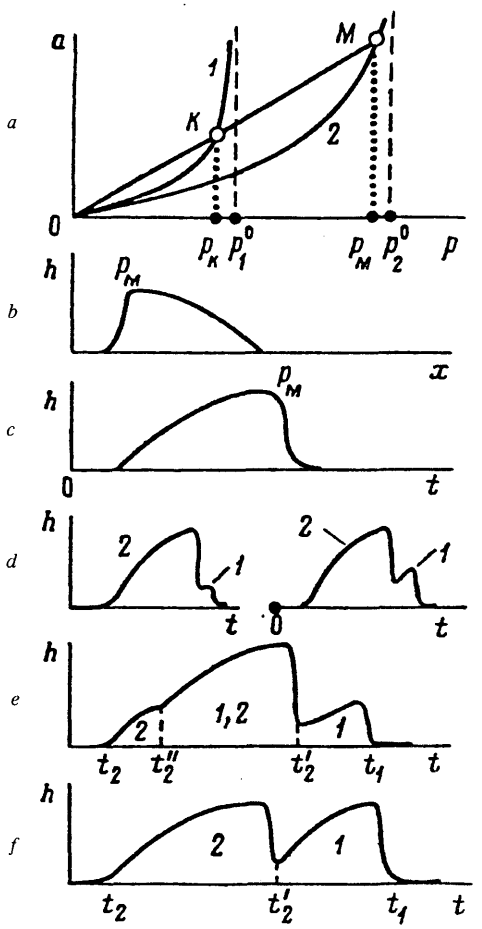



Figure 10. Schematic illustration of the CNSV process:[15] *a*) sorption isotherms for components *1* and *2* to be separated; *b*) distribution of the component along the bed; *c*) CDG for a single component; *d*) the possible CDG in the enrichment of the impurity; *e*) CDG for partial separation of the mixture; *f*) CDG for complete separation of the mixture.

It is known from the general theory of chromatography[56,88] that, under the conditions of concave sorption isotherms, the band of the substance analysed should have a greatly diffuse leading front and a cut-off rear edge (Fig.10*b*). A diffuse "tongue" and an abruptly terminated "tail" are recorded on the elution curve (Fig.10*c*). Chromatograms of this kind are observed in gas–liquid and gas–adsorption chromatography at concentrations close to saturation. The injection of large samples into the chromatographic column leads to concave sorption isotherms both for the solvent *2* and for the impurity *1*. The rate of migration of the points in the leading diffuse front along the bed is described by the derivative of Eqn.(1), while the rate of migration of

the curtailed rear edge along the bed is determined, in conformity with the material balance, by the slope of the straight line *OM* (Fig.10*a*) drawn from the origin of coordinates *O* through the point *M* corresponding to the maximum concentration at the front. The straight line *OM*, drawn for the rear edge of the more volatile component *2*, intersects the isotherm of component *1* at the characteristic point *K*. All the points in the leading front of component *1*, for which the derivative is less than the slope of the straight line *OM*, move along the bed faster than the rear edge of component *2* and can therefore catch up with it. This leads to the "limiting effect"—component *1*, dissolving at the rear edge of the limiter *2*, is retarded and concentrated. According to the material balance at the zone boundary, the following equation should hold:

$$a_2/c_{2M}=a_1/c_{1K}, \qquad (17)$$

where $c_{1K}$ and $c_{2M}$ are the concentrations in the gas phase corresponding to the points *K* and *M* and $a_1$ and $a_2$ are the degrees of adsorption at these concentrations. It must be emphasised that the final result of the enrichment is determined by the isotherms of the individual components and is independent of the character of the solutions formed in the intermediate zone between the components. The chromatogram of the less volatile impurity component *1* can have either the stepped form, when the initial concentration was smaller than at the point *K*, or can have a growing leading front in the opposite case (Fig.10*d*). However, in both cases Eqn.(17) should hold for the concentrations at the rear solvent boundary.

The advantages of the injection of large samples into a column with a SP for the separation of mixtures have been demonstrated.[5,15,17] It is known[56,57] that an increase of the dose in traditional chromatography leads to the overloading of the column and to the impairment of the separation owing to the overlap of the peaks. However, further increase of the dose makes it possible to attain operating conditions where CD effects exert an influence. The influence of the interaction of sorbate molecules not only with the SP but also with one another is then manifested. In contrast to CD, in the CNSV there is a possibility of using the sorbent selectivity for the improvement of the separation. The temperature gradient and the limiter promote the occurrence of distillation processes. The action of all the remaining auxiliary separation factors has been illustrated by means of examples.[5,15] Thus, after the injection of 0.1 ml of a liquid heptane–cyclohexane mixture into an isothermal column (at 10 °C) with tricresyl phosphate, a chromatogram similar to that illustrated in Fig.10*e* is obtained. The frontal processes at the leading and rear edges of the band lead to the partial isolation of the components, while the intermediate zone contains the unseparated components *1* and *2*. The use of a negative temperature gradient (from 75° to 10 °C) makes it possible to attain complete mixture separation (Fig.10*f*). From the standpoint of traditional chromatography, this result is paradoxical, since an increase of column temperature should impair the selectivity of the separation. The results obtained are associated with the CD processes on the SP. An analogous effect is attained by employing a limiter. In contrast to CD, in the CNSV there is a possibility of the separation of azeotropes or systems which are otherwise difficult to separate. This has been demonstrated[5,15] in the separation of the heptane–isooctane and benzene–cyclohexane mixtures on α-iodonaphthalene as the SP. Whereas the components are not separated under isothermal conditions (0 °C) for a dose of 0.04 ml, the application of a gradient (85–0 °C) leads to complete mixture separation.

CNSV processes are manifested and are used in the concentration and determination of impurities. A short (20 cm) chromatographic column with a thermal pulse has been used[44] at the concluding stage after repeated CD accumulation of $C_9$–$C_{11}$ alkane impurities in heptane. The lowest concentration which could be determined with the aid of a katharometer was $10^{-3}$ vol.%.

In order to transfer the impurity from the preliminary CD column to the next, separating CC, it is necessary to create favourable conditions for the occurrence of the CNSV. In the analysis of the butanol impurity in water[51] without a limiter (ethanol) or under conditions which rule out the condensation of the alcohol (CC heated above the $t_b$ of ethanol), highly diffuse butanol peaks appear on the chromatogram. In this case the butanol band passes from the CD column to the CC in a large volume of gas (20 ml). If a temperature difference is maintained between the columns (from 70° to 20 °C), ensuring the condensation of ethanol in the initial section of the CC, then the width of the butanol peak on the chromatogram diminishes by a factor of 7. The possibility of combining a CD pre-column with the CC in order to increase the size of the injected sample at least by an order of magnitude was demonstrated in the same study.

The role of the SP in the concentration of impurities from a large sample has been discussed briefly.[72] Harris[107] considered the influence of large samples injected into a column with a SP on the retention of the component under the conditions of marked deviations from Raoult's law. Taking into account the dependence of the activity coefficients on the mole fraction of the component in solution, the author determined qualitatively the character of the change in the retention volume of the impurity with change in the size of the dose. In fact Harris[107] stated the necessity to take into account the intermolecular interaction in the complex system comprising the components of the mixture to be analysed and the SP and the influence of this interaction on the results of the separation. It has been shown[77] that the presence or absence of the SP on the initial section of the CC does not affect the shape of the peaks when the latter spread. This is associated with the presence of a large amount of the solvent, which predominates along the section and forms an unusually large film. However, for comparable amounts of the SP and the solvent, their mutual influence on the isolation of the impurities is manifested.

A suitable solvent was selected[79] for the injection of the sample using the SE and it was established that there must be a definite correspondence between the polarities of the SP, the solvent, and the sorbate.

Jenkins[108] made a special study of the influence of solvent polarity on the shape of the peaks for the direct injection of the sample into the CC. A new method was developed involving the preliminary injection of an additional solvent:[73] several solvent samples were introduced by a single syringe using an air gap to separate different solvents. It was established[108] that the use of non-polar sorbates (alkanes) for injection in a polar solvent (methanol) leads to symmetrical peaks on silicone phases (of the type of SE 30 and 52). The use of a weakly polar secondary solvent (cyclohexane), which is injected before and after the main sample and forms an azeotrope with the first solvent, makes it possible to isolate alkanes in the form of narrow peaks. The solvent evaporation processes occurring are similar to azeotropic distillation.

A number of methods for "correcting" the shape of the peaks, corresponding to our ideas about the CNSV process, have been proposed.[102,108] It has been noted that polar compounds in a polar solvent have normal peaks, but the

shape of some of them is distorted. This is associated with the fact that the condensed solvent prevents the penetration of non-polar substances to the SP on the surface of the CC. In order to improve the process, it is recommended that one should use a mixture of solvents forming an azeotrope, which is equally permeable to both polar and non-polar substances. The prospects for the employment of two solvents simultaneously in order to elucidate whether the split peak corresponds to one substance or several substances have been discussed.[102]

In the course of several years, starting in 1976, a number of studies on the effects occurring in gas-liquid preparative chromatography when samples with a large content of the main component are injected have been published.[109-112] A number of characteristic features of the CNSV considered above and observed in the isolation of impurities from *m*-xylene (dose volume up to 10 μl) on a 640 × 1.4 cm column filled with Spherochrome with the PEGA 25% phase have been noted: for concave *m*-xylene sorption isotherms, an extended leading front of the main component is observed, while the rear edge is sharply cut off, which promotes a clear-cut isolation of the impurity; an increase in sample size shifts the retention times of the impurity components; the observed decrease of the width of the impurity peak following the main component, compared with the injection of an equal amount of an individual impurity component, has been observed.

The last two factors leads to a sharp increase of the formal HETP (by a factor of 10–20), which was also noted by Berezkin[113] and was discussed in Section III of the present review. This treatment of the mechanism of the phenomena occurring is close to that put forward by Jennings[60,89] and Grob[52,79] and is based on the consideration of the elution of the impurity band against the background of a binary solution with a concentration gradient of the main component in the SP.[114] It has been noted[109] that the transfer of the impurity in the field of a variable sorption capacity is analogous to the processes occurring in non-stationary chromathermography. Considering the processes from the standpoint of GLC, Mar'yakhin and Vigdergauz[109] clearly formulated the idea that the main component can play the role of the "sorbate-concentrator" (in other words the limiter). The sooner the impurity is eluted after the main component, the greater the increase in concentration under these conditions. It has also been noted that the main component can be introduced after injecting the mixture containing the components to be concentrated. It is convenient to use a main component which is not recorded by the detector. These features of the CD methods for the concentration of impurities (in the absence of a SP on an enrichment column) were used in our later investigations.[43-45]

The mechanism of the formation of a narrow zone of the impurity component under CNSV conditions, determined by the occurrence of frontal-sorption processes on the SP, has been confirmed in a series of studies published in 1983.[70,71,99-101] The authors investigated experimentally the band forming processes on two sections of the initial part of the CC. On section I (Fig.5), the SP is saturated by the solvent vapour. As noted above and demonstrated in a number of studies,[10,21,49,72] after the elution of the sample from the section I, not all the impurity substance is contained on the rear edge of the solvent. The complete isolation of the impurity component in the form of a single peak is attained by employing a limiter. However, in a number of experiments also without the limiter a complete isolation of the impurity in the form of a sharp peak has been observed on the chromatogram—this occurs in the subsequent separation of the injected sample on the SP in the CC. In order to investigate the process mechanism, a detailed experiment has been performed in which the distribution of the substance along the bed was determined.[70] A 20 m column consisted of a short etched capillary (1 m) and 15 sections on which a SP (OV-1) was deposited and which were connected by Teflon tubes. Some time after the injection, the column was taken apart and the sorbate contained in the part of the CC located between the injector and the disassembly point was blown out into the atmosphere. The CC was then reassembled and the chromatographic process was completed. The large number of disassembly points in the first half of the CC and experiments carried out with a shift of 2–15 s made it possible to obtain a detailed picture of the change in the distribution of the sorbate along the bed as a function of time. The results obtained can be represented by means of the series of diagrams in Fig.11. On the elution curve for the impurity extracted from the first section, a low "base" (110 s long) is observed, while at the end of the zone there is a narrow "tower" (5 s long), whose area corresponds to 70% of the injected octane. This result is fully consistent with the above description of the elution curves obtained on an inert carrier.[10,72] The theory of this process was examined by ourselves in a study of the isothermal CD elution of a mixture[21] (see above).

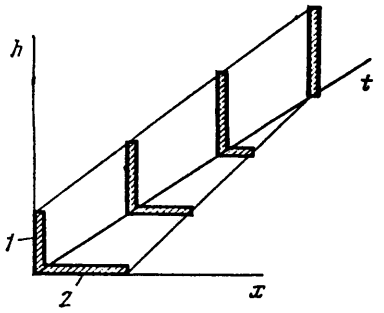



Figure 11. Distribution of the sorbate along the section of the column with SP at different times;[70] $h$ = height of band on the bed; $x$ = width of band: 1) "tower component"; 2) "base".

The experiments[70] in which the movement of the sorbate along the SP in a CC was investigated have shown, over the first 0.8 m, that the band consisting of a planar "base" and a narrow "tower" migrates almost without change. Then, over a section of the CC between 2 and 5 m from the origin, the "base" is rapidly shortened as a consequence of the increase of the area of the "tower" part of the peak and towards 6 m the entire substance is concentrated in a single narrow peak. This result has been confirmed by data obtained by comparing the rates of migration of the leading edge of the "base" of the octane band and of its rear "tower" component. Over the first 5 m, the "base" migrates at a rate of 2.4 cm $s^{-1}$, which is associated with its presence within the limits of a zone with a high content of the solvent. At a distance of 5–6 m from the start of the CC with a SP, the rate of migration of the leading octane front increases to 8.5 cm $s^{-1}$, corresponding to a linear rate of migration of octane along the SP in the complete absence

of the solvent. The "tower" component of the band passes slowly only over the first 2 m and then, at a distance of 2–3 m from the start of the CC, it acquires the maximum rate of 9 cm $s^{-1}$, which enables both fronts to be united after 3.3 min in the vicinity of the 6 m marker. The passage of the sorbate band through a narrow rear edge of the solvent leads, according to the authors,[70] to a concentrating effect. Initially the solvent band migrates more slowly than the sorbate band, which adjoins, via its "tower" component, the rear edge of the solvent over a long period. This can be seen from plots of the migration (Fig.12). Over the section from 2 to 5 min, the rear edge of the solvent begins to overtake by 2–3 s the rear edge of the impurity. During this period, both rear boundaries (of the solvent and impurity) are accelerated and in the vicinity of 5 m they combine with the leading boundary of the impurity, which migrates slowly within the limits of the solvent-saturated SP. Next, the rear solvent edge overtakes both boundaries of the impurity band and continues to migrate along the column. In short columns (5–10 m) an impurity peak 0.6–1.1 s wide was obtained directly behind the solvent zone after 3–5 min.

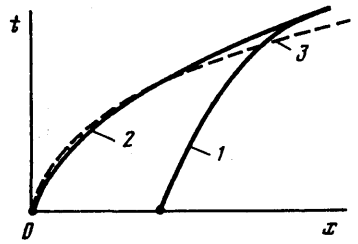



**Figure 12.** Graphical representation of the movement of the sorbate and solvent edges:[70] 1) and 2) leading and rear sorbate edges; 3) rear solvent edge.

It has been emphasised[71] that the concentrating effect on a solvent-saturated SP is associated with the difference between the rates of migration of the solvent and sorbate edges. The reduced rate of migration of the rear solvent edge accompanied by a high rate of migration of the sorbate along the solvent-free SP in fact leads to the compression of the band from 120 s to 1 s. The authors calculated the retention coefficient $K_{ret}$ defined as the ratio of the rates of migration of the sorbate along the SP in the presence and absence of the solvent. In experiments with repeated successive injection of the sample and additional "supply" by the carrier gas saturated by the solvent vapour, a study was made of the dependence of $K_{ret}$ on the nature of the SP, the solvent, and the sorbate. When solutions of decane in pentane ($1:10^3$) were injected at 3 min intervals, individual decane peaks, moving in succession at intervals of ~60 s ($K_{ret} \cong 3.5$) were observed. Analogous results were obtained in differential CD[16] with solutions of volatile components which were used instead of SP. It is noteworthy that the injection of a dose of the pure solvent makes it possible to select experimental conditions such that the impurity can be collected in the form of a single peak from several successive injections of the sample.[44]

We reached previously[2,9,15] the conclusion that the zone boundaries should adjoin on the basis of the study of the concave sorption isotherms of the components. The mechanism of the concentrating effect can be accounted for by the occurrence of a limiting process in CNSV. As the solvent band moves, it spreads and the concentration at the maximum on the curve falls. The increase of the rate of the sharp rear edge of the band is associated with the decrease of the slope of the *OM* secant on the plot of the sorption isotherm (Fig.10*a*). The solvent *2* therefore initially functions as a limiter until the secant drawn from the point *M* on the solvent sorption isotherm (corresponding to the maximum concentration) intersects the sorbate (impurity) sorption isotherm *1*. This period is in fact responsible for the effect involving a sharp increase of the concentration. It follows from this explanation that the impurity concentrations in the gas and liquid phases should increase. As the solvent migrates along the layer of SP, its concentration at the maximum falls and it moves ahead as the lighter component, while the concentrated impurities migrate in narrow bands further along the column in accordance with their partition coefficients in the SP.

The study of the mechanism of the concentrating process on the basis of the sorption isotherm makes it possible to predict the final result of the enrichment of the impurity at the rear solvent edge. This does not rule out the approach associated with allowance for chromatography on the SP with a gradient distribution of the latter. However, in this case it is essential to consider the movement of the SP along the bed. Certain quantitative relations describing the migration of the sorbate fronts at high concentrations have been published.[15]

## VII. DEVICES FOR THE INJECTION OF LARGE SAMPLES AND THE RESULTS OF THEIR APPLICATION

The direct injection methods examined above require the creation of new designs of injectors. In the present Section we shall consider only the injectors in which the sample injection is accompanied by the formation of a large amount of liquid in the initial section of the column where the CD processes are manifested. The injection system and the method of injecting substances in many respects determine the quality of the separation. When a highly effective injection system is used, the following requirements must be met:[97] the absence of the overlap of the solvent peak with the peaks of the components to be separated; the elimination of the fractionation of the sample components; the reproducibility of the injection times with a relative standard deviation less than 0.1%; the reproduction of the normalised peak areas with a relative standard deviation less than 1%; the reduction to a minimum of the thermal decomposition and sorption processes as well as reactions; the constancy of the column efficiency; quantitative and representative extraction of both impurity and main sample components; independence of the injection processes of the operating conditions of the column.

In the studies on the CD determination of impurities[43–51] the sample was injected into the column through the usual injectors used in commercial chromatographs (Tsvet-100, LKhM-8MD, etc.). The initial section of the column (about 10 cm) was located in the evaporator of the injector and the sample was injected by means of a syringe directly onto the bed. Glass and metallic U-shaped and spiral CD columns, up to 3 m long and 2–4 mm in diameter, filled with metallic or etched glass beads (0.25–0.5 mm fraction) were employed.[44,45,49,50] In experiments designed to

isolate impurities under the conditions of thermal CD, a temperature field with a negative gradient was created along a section up to 1 m long. The gradient was established by employing a furnace with a variable-pitch nichrome spiral winding. The temperature along the field was varied from $t_b$ for the solvent to room temperature. The temperature in the evaporator was kept somewhat below $t_b$ of the solvent (Fig. 9d) in order to prevent the entry of the sample into the inlet connectors, since the injection of large amounts of liquid into a strongly heated column entails an increase of pressure. The use of a preliminary CD column made it possible (with the aid of a switching tap) to inject samples with volumes up to several millilitres.

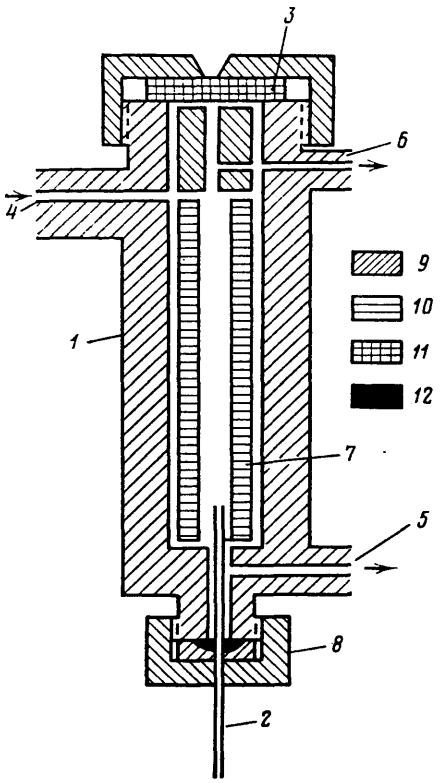



Figure 13. Schematic illustration of the evaporating injector for the splitless introduction of the sample:[52] 1) evaporator; 2) CC; 3) septum; 4) and 5) entry and exit of carrier gas; 6) flushing of the septum; 7) insert; 8) attachment of the CC; 9) metal; 10) glass; 11) rubber; 12) graphite.

Special injectors have been developed for the direct splitless injection of samples into a CC. The sample was initially[52] injected from the usual injectors (Fig. 13) in which the carrier gas disposal line 5 was initially closed during the transfer of the sample from the evaporator to the CC. In order to eliminate the influence of the septum 3 of the injector, a special device with a controlled leakage of the gas has been used.[5] The Carlo Erba Company later designed an injector[52,55] where the septum was in contact with a separate stream 6. The advantages of splitless injection have been demonstrated in analyses of an admixture of benzene and pentane (0.01 p.p.m.), steroids, and the components of tobacco scent and tobacco smoke. Injection without stream splitting has been used successfully for the analysis of natural scents and specimens of the ambient medium.[79] The Hewlett Packard Company has published manuals for the use of commercial injectors in routine analyses.[89]

Having analysed the system for injection into CC existing at the time, Yang et al.[97] concluded that the best injection system is one without stream splitting.

Data for the reproducibility of the injection method without stream splitting have been obtained[97] using the automatic injector of the Varian-3700 apparatus in relation to the analysis of a mixture of $C_{13}$–$C_{32}$ n-alkanes with the temperature programmed in the range from 120° to 280 °C. The solvent was n-decane. The relative standard deviation of the retention time based on the results of 11 measurements was on average 0.05% and that for peak areas was 1%. The optimum parameters were chosen[97] using a simplex experimental design method. It has been suggested that one should be guided by the following rules for the selection of the parameters: sample size from 0.1 to 10 μl; rate of sample injection about 1 μl $s^{-1}$; sample injection time more than 20 s; time during which the blower is switched on after injection more than 40 s; effective dynamic range of sample dilution $10^5$: 1; evaporator temperature not more than 230 °C (for solvents with $t_b$ < 100 °C); the solvent should have $t_b$ smaller by 25 °C than the $t_b$ of the lightest component to be determined, since otherwise it is lost together with the eluted solvent; the initial constant temperature should be lower by 15–30 °C than the $t_b$ of the solvent; the components evolved before the solvent can be determined quantitatively only when their relative capacity is sufficiently different from that of the solvent.

The splitless conditions ensuring the entry of 95% of the sample into the CC have been investigated.[115] The injector produced by the Carlo Erba Company for models 2900 and 4160 was used.

The injection of large samples (up to 50 μl) of solutions of $C_{11}$–$C_{16}$ n-alkanes containing pesticides into large-diameter (0.77 mm) CC using an electron capture detector has been described.[98] The injection system, described by Grob and Grob,[52] in which the values for the ejection of the stream and for the flushing of the septum were closed throughout in order to eliminate the possible losses and to ensure the constancy of the flow rate through the column, was used in the above study on the basis of the Varian-1400 apparatus. Since the injection of large samples distorts the peak retention times, the results of the analyses were characterised by the separation factor $K_1$ for the DDT pesticide vapour. The relative standard deviation in the determination of $K_1$ varies from 1.5 to 5.5% depending on the solvent selected. The maximum value of $K_1$ was obtained when a 2–4 μl sample was injected. On further increase of sample volume, no significant decrease of $K_1$ up to 100 μl was observed.

In a number of instances where a SP is used, it is possible to achieve injection with stream splitting.[68] This permits a decrease of the stream splitting coefficient and hence an increase of the amount of sample injected. By virtue of the decrease of the volume of the vapour on condensation, the additional amount of substance is as it were "sucked"

onto the column. Under such conditions, the stream splitting coefficient is more stable and does not change during the injection period.

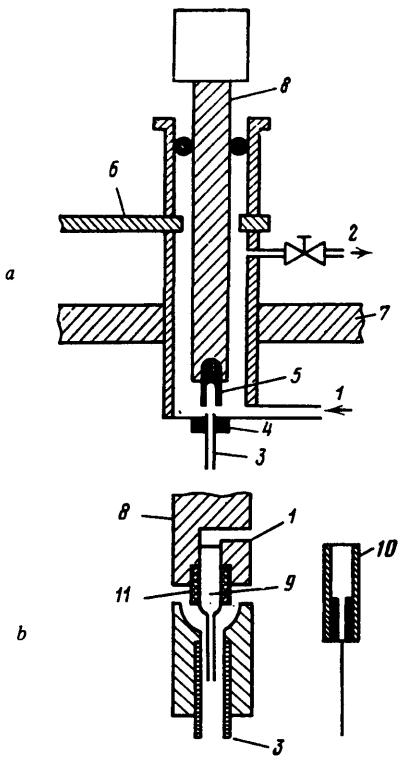



**Figure 14.** Schematic illustration of the injector for the direct introduction of the sample into the CC:[117] *a*) "macro"-version; 1) and 2) entry and exit of carrier gas; 3) CC; 4) seal; 5) crucible; 6) valve; 7) insulation of the thermostat; 8) valve shaft; *b*) "micro"-version: 9) and 10) micropipette; 11) silicone rubber.

Schomburg et al.[116-118] were the first to point out that the splitless method employing an evaporator is irrational. This is because ultimately one has to inject the initial liquid sample directly into the CC; for this reason the intermediate operations involving evaporation and condensation are superfluous in splitless injection. The disadvantages characteristic of the usual injection systems with stream splitting can then have an effect. Schomburg was the first to employ the direct injection of liquid into CC of normal size (0.3 mm) and described two designs for injectors:[117,118] the "macro"- and "micro"-versions. In the first case (Fig.14*a*) a 5–10 μl sample is placed in a small glass crucible *5* attached with the open end downwards to the shaft *8* of a sliding valve *6*. The shaft is exposed to the carrier gas which flows along line *1* in the CC *3*. In order to inject the sample, the liquid in the crucible *5* is brought into contact with the end of the CC. Under the influence of capillary forces, the liquid to be injected enters the CC. In the "micro"-version of the direct method (Fig.14*b*), the extended end of a micropipette (with a volume of several nanolitres) is inserted into the CC with the aid of the same valve *6*. The carrier gas blows the liquid into the CC. Special care must be taken to ensure that the CC and the pipetter are coaxial. The characteristics of the three injection methods (with and without stream splitting and also the direct method described) have been compared. The relative standard deviation (reproducibility error) in the determination of the composition of a mixture of $C_{18}$–$C_{34}$ n-alkanes was not worse than 1% for all the methods. Two completely identical chromatograms for the analysis of the products of the Fischer-Tropsch reaction with a dose of 1 μl have been published. In the direct injection, the sample was diluted by a factor of 100 with octane and in injection with stream splitting the splitting coefficient was 1:100. Direct injection has the following advantages:[118] the separate evaporator unit with all its disadvantages (superfluous volume and surface, selection of flushing conditions, and the creation of a uniform gas mixture) is eliminated, there is no rubber septum, there is no need for a syringe, and there is no stream splitting. The disadvantages of the direct injection include the contamination of the inlet section of the CC by involatile sample components, the washing off of the SP, and the difficulty of replacing the injected volume.

The methods for sample injection with stream splitting have been criticised[67] and conclusions similar to those of Schomburg and co-workers[116-118] have been reached. In a general assessment of the methods of injection with stream splitting, it has been concluded[63] that the reproducibility is excellent but the results are poor.

Another version of the direct injection of the sample into the CC (Fig.15), differing from Schomburg's method by the fact that the injection is via the usual microsyringe through a special valve[119] without a septum, has been achieved.[63] Initially the needle of the syringe, whose outer diameter is smaller by 0.05 mm than the inner diameter of the CC (0.3 mm), is inserted in the channel *5* of the injector up to the shaft of the valve *4* sealing hermetically the channel. The shaft is then moved back and a small controlled ejection into the atmosphere is established in the gaps between the walls. The syringe is lowered and the needle is inserted into the CC via the guiding channels *3*. Samples with a volume of 0.1–0.2 μl are injected rapidly and those with larger volumes are injected at a controlled rate. The injector is placed in an insulating beaker with air cooling. The volume of the sample injected can be measured with the aid of such a device and the rate of supply of the sample, the cleanness of the surface, etc. can be monitored. The continuous operation of the injector described in the course of a year confirmed its advantages and led to an insignificant modification:[94] the lock nut was replaced by a two-position Teflon tap (open-shut) and cooling was achieved by means of a radiator exposed to air from the thermostat ventilator.

The results of the analysis of dilute solutions of polynuclear aromatic compounds in methylene chloride showed[67] that the relative standard deviation in the determination of the content of substances with the aid of the injector developed is 3–5%, which is smaller by a factor of 4–5 than the value obtained with the aid of an evaporating injector. The results of the use of the above system for the analysis of thermally unstable compounds—mustard oil and wide-boiling fractions of the methyl esters of $C_8$–$C_{22}$ aliphatic acids—are quoted in the above study. The

relative standard deviation was 1.2–1.7% and was respectively smaller by factors of 3 and 5 than in injection with and without stream splitting.

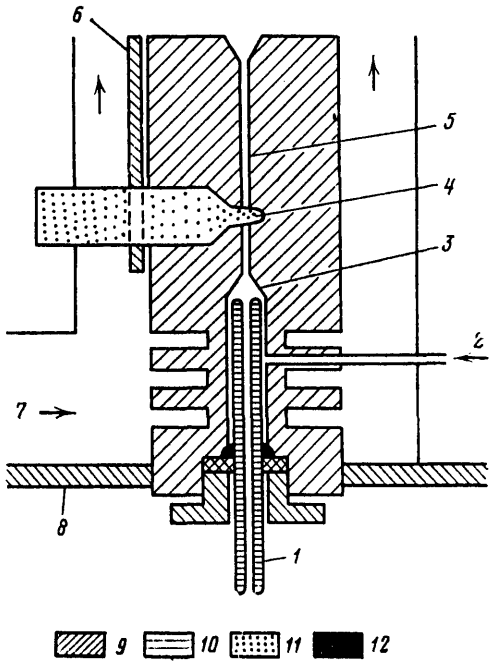



**Figure 15.** Schematic illustration of the injector for the direct introduction of the sample into the CC:[94] 1) CC; 2) entry of carrier gas; 3) centreing cone; 4) closing valve; 5) membrane replacement channel; 6) valve spring; 7) entry of cooling air; 8) thermostat insulation; 9) metal; 10) glass; 11) Teflon; 12) graphite.

The direct injection method[120] has been used as a reference procedure for the estimation of the accuracy of injection by other methods employing stream splitting after the evaporation of the sample. The technique of sample injection from a syringe was varied (cold and hot needle, air or solvent plug). In most cases concordant results were obtained for $C_9$–$C_{20}$ alkanes, while for high-molecular-weight hydrocarbons close to $C_{44}$ the usual method leads to losses of the test substance amounting to 25–75%. The authors believe that the components of a mixture with a wide boiling range are fractionated on the hot needle of the syringe. When the needle is heated to a temperature exceeding the $t_b$ of the solvent, the high-boiling components are concentrated on the liquid meniscus at the piston and do not reach the CC. This required a change in the technique of direct injection onto the column[67] (also using a syringe) in the part concerned with the improvement of the cooling system.[103] In the "Fractovap" model 4160 injector,[121] provision is made for additional channels to allow the passage of cooling air and a heat exchanging insert is placed in the connecting ring, which makes it possible to cool the CC from the inlet to a distance 10 mm below the level of the column thermostat.

The accuracy and reproducibility of the injection by three methods (direct injection onto a cooled column and injection with and without stream splitting) were compared in the analysis of samples containing extremely high-boiling compounds—triglycerides.[122] The samples were prepared in hexane with added pentadecane as the standard. Direct injection onto the cooled column (modified version of the injector[103]) ensured the best results—the relative standard deviation in the determination of the peak area did not exceed 1–3%. However, the losses calculated taking into account the sensitivity of the flame-ionisation detector ranged from 3 to 10%. When the injection technique without stream splitting, described by Grob and Grob,[123] was used with evaporation of the sample at 400 °C, the losses of the test substance were even greater (14–20%) and the reproducibility of the analyses was to within 9–13%. The usual injection method with stream splitting yielded unsatisfactory results. The losses of the test substance increased to 25–50% and the error in the reproducibility rose to 15–30%. The causes of the errors in the method involving direct injection onto a cooled column have been examined.[104,124] Attention has been concentrated on the stage involving the transfer of the liquid from the syringe needle onto the inner surface of the CC wall. It is emphasised that this must be a purely mechanical process without evaporation. The partial loss of the components is ruled out when the syringe plunger is moved rapidly (several metres per second). Injection of 1 μl samples (from a 10 μl syringe) showed that appreciable losses of $C_{20}$ and $C_{28}$ n-alkanes (in hexane and pentane) are observed for an injection time reaching 1 s. Use of 0.5 μl syringes proved unsuccessful. Direct injection onto a cooled column permits an extensive variation of the sample volumes. The upper limit is determined by the risk of washing off the stationary phase and the lower by the possibility of the incomplete transfer of the sample from the syringe. An increase of column temperature diminishes the extent of the washing off of the stationary phase but, as the $t_b$ of the solvent is approached, it induces the reverse flow of the test substance from the CC. In order to avoid contamination of the column by the stationary phase, the phase is first removed from a large section of the column. A reasonable maximum dose for CC is 10 μl. When pentane and an initial temperature of 30 °C were used, a relative standard deviation of 0.3–1.5% was obtained without an appreciable loss of the component. The minimum permissible dose was 0.2 μl and satisfactory results were obtained with large 5 and 10 μl syringes. When the column temperature (140 °C) exceeds the $t_b$ of the sovent (hexane), the sample is appreciably condensed on the outer walls of the needle even under the conditions of rapid injection (the losses reached 20%); if the time during which the needle remains in the injector is 5 s, then the losses are doubled. The possible operating conditions involve a temperature of the CC slightly exceeding $t_b$—by 7 °C for pentane and hexane.

The test of the operation of the usual injectors with heated septums showed that, when syringes (with any injection technique) and systems in which the sample is evaporated are used, it is impossible to avoid a partial loss of the components ($C_{20}$ and higher alkanes).[125] The only reasonable alternative involves direct injection onto a cooled column.

Galli and Trestianu[104] paid particular attention to the selection of operating conditions preventing the "ejection" of part of the sample from the CC in the direction opposite to that of the flow. Knauss et al.[126] considered the

mechanism of the distribution of liquid along the initial section of the CC under the conditions of a temperature gradient. Badings et al.[127] and Chaudhan and Darbre[128] described designs for glass direct injection devices. A comparative study has been made[129] of various types of injections: direct injection with a crucible—the "macro"-version (Fig.14); direct injection using a syringe and an injector (Fig.15) with additional cooling; injection with stream splitting and injection without stream splitting using a standard injector (Fig.13). Both direct injection methods yield satisfactory results. The version with the crucible is technically simpler, but leads to a greater error—the relative standard deviations in the determination of the area are respectively 2.5 and 0.7. When these methods were used to determine the sensitivity coefficient of methyl octanoate (in relation to n-dodecane) the relative standard deviations were 0.25 and 0.14% respectively. Schomburg et al.[130] estimated the level of losses of $C_{10}$–$C_{40}$ alkanes when a stream splitter was used. The application of a dodecane instead of an octane sample as the solvent and reduction of the evaporator temperature from 310° to 210 °C made it possible to increase the $C_{40}/C_{13}$ peak area ratio from 0.13 to 1.02.

Comparison of the direct injection methods with and without stream splitting demonstrated a statistically significant difference between the reproducibilities and accuracies of the analysis of 10 aliphatic acids (from $C_{16}$ to $C_{22}$) in rape seed oil.[131] The relative error was on average 2.3% for the direct method and 6.4 and 6.0 respectively for injection without and with stream splitting.

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A review of studies on injection methods for the determination of impurities shows that the mechanism of the processes occurring is in fact related to the new separation method introduced by the present author,[1-9,15-51] namely chromadistillation (CD), which takes place along the initial section of the column. All the existing methodological versions of CD have found an application: isothermal elution, limiting chromatography, CD, the chromatography of nearly saturated vapours, and thermal CD.

Analysis of a fairly large number of publications on the "solvent effect" has shown that their authors actually arrived at the conclusion that the CD principles must be employed. Studies on the SE constitute an important step forward in the field of injection. It has become possible to introduce samples up to 10 μl into capillary columns, whereby the accuracy of the results has been improved. A further significant (by two orders of magnitude) increase of the sample injected (and hence of the sensitivity of the measurements) is possible as a result of the employment of special CD pre-columns or injectors. The CD theory helps in the formulation of the principal requirements ensuring the optimum operating conditions of the injection system: the sample must be introduced directly (without preliminary evaporation) into the column under the same conditions as the mixture to be analysed and the injecting syringe, and the site of injection must have a sufficiently large volume (0.2–1 ml) to permit the distribution of the sample; along the sample distribution section, it is essential to create conditions for the repeated condensation of the mixture components—a temperature gradient must be set up (with a decrease of temperature from the closest possible value to the $t_b$ of the solvent) or an additional solvent must be introduced. The above description makes it possible to improve the design of the injector for capillary and packed columns.

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# The Synthesis of Lepidoptera Pheromones

E.D.Matveeva, A.L.Kurts, and Yu.G.Bundel'

The review surveys the data in numerous publications of the synthesis of the pheromones of scale-winged insects (Lepidoptera). Attention is concentrated on problems of the sterospecific synthesis of pheromones.
The bibliography includes 217 references.

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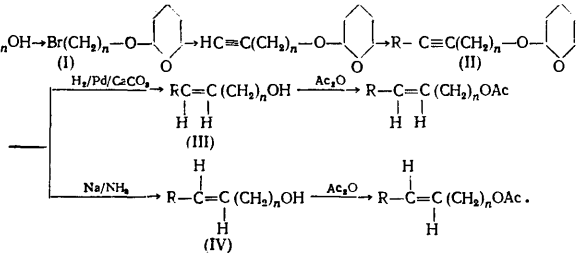
During recent years, several new promising trends have arisen in the fight against harmful insect species, involving high selectivity and also virtually complete safety for man and warm blooded animals. In the first place one should include among these, methods based on the employment of biologically active substances—pheromones. Pheromones are chemical substances secreted by insects and inducing specific behavioural and physiological responses in other insects exposed to them. Among the pheromones known at the present time (sex pheromones, tracking pheromones, aggregation pheromones, food pheromones, and fear pheromones), the sex pheromones appear to be the most promising. Their exceptional biological activity and species selectivity give rise to the hope that they may be used in the active suppression of the multiplication of pest populations without contaminating the biosphere and without disturbing the biological equilibrium in nature, and also as a means for the operative allowance for the number of pests present. Extensive experimental data devoted to the identification, synthesis, and applications of insect pheromones have accumulated during the last ten years. These data have been surveyed in a number of reviews[1-4] and a monograph,[5] but most studies have been published during the last four years.

This review is devoted to the synthesis of insect sex pheromones and embraces mainly the studies during 1970 to 1983. All the reviews considered deal with scale-winged insects (Lepidoptera). These compounds are unsaturated aliphatic alcohols, acetates, and aldehydes,[1,2,5] but recently ketones have also been isolated and identified.[6] The difference between their structures is one of the principal factors in the reproductive isolation of insects. It has been found recently that Lepidoptera pheromones are multicomponent mixtures of compounds:[7] certain insect species secrete mixtures of *cis*- and *trans*-isomers as pheromones,[8] while others secrete a mixture of aldehydes,[9] an acetate–aldehyde mixture,[10] or other mixtures.[11] An attractant for one insect species can be an inhibitor for another; thus the attractant of *Paralobesia viteana*—*cis*-dodec-9-enyl acetate—inhibits the attracting activity of *Phyacionia buoliana*.[12] The quantitative ratio of the components in such mixtures is an important factor which enables sympatric insect species (species living in the same area) to avoid cross breeding.[13]

For the majority of representatives of Lepidoptera, the ratio of the *cis*- and *trans*-isomers in the mixture is important. For example, *cis*-dodec-8-enyl acetate is an attractant for the oriental fruit moth *Grapholitha molesta*, but the greatest attracting effect has been observed in the presence of 7% of the *trans*-isomer;[14,15] for the males of the European pine shoot moth *Rhyacionia buoliana*, the greatest activity has been shown by the mixture of *trans*-dodec-9-enyl acetate and 1.15% of its *cis*-isomer.[16] The high species specificity of pheromones is achieved precisely by the exact proportions of geometrical isomers, which requires appropriate methods of synthesis and a high degree of chemical, geometrical, and stereochemical purity.

## I. MONO-OLEFINIC ALCOHOLS AND ACETATES

One of the commonest methods of synthesis of pheromones involves the use of mono- or di-substituted acetylenes as key compounds. Thus about 100 unsubstituted unbranched $C_{10}$–$C_{16}$ compounds containing a terminal triple bond and the acetate group have been synthesised by Japanese investigators.[17] Screening led to the discovery of substances attracting specifically 93 species of insects belonging to 15 Lepidoptera families of Japan (the *Torticidae*, *Noctuidae*, etc. families). All the specimens were synthesised in accordance with the following scheme:



The complex of lithium acetylide and ethylenediamine was condensed in THF, HMP, and HMP/THF with the corresponding tetrahydropyranyloxyalkyl bromide (I) in order to obtain an almost quantitative yield of the key compound—a disubstituted acetylene (II), which was subsequently hydrogenated over the Lindlar catalyst to obtain a product containing more than 95% of the *cis*-isomer (III). The corresponding *trans*-isomers (IV) were obtained by reduction with lithium in liquid ammonia.

A classical method for the synthesis of mono-substituted acetylenes involves the splitting off of hydrogen halides from the corresponding halogenoethylenic compounds.[18] The hydrogen halide is usually split off by means of a potassium hydroxide solution in absolute ethanol, ethylene glycol, and

cellosolve, a potassium hydroxide melt,[19] or sodium in liquid ammonia or in the form of a suspension in a mineral oil.[20–22] Here one must bear in mind that the classical version of the dehydrohalogenation reaction leads to the migration of the triple bond into the interior of the molecule,[23] while the use of sodium amide in a mineral oil has the opposite effect of shifting the triple bond to the end of the chain.[23] A modified method, based on the use of a suspension of fine ground KOH in dimethyl sulphoxide (DMSO), is more effective. The terminal acetylene is thus obtained in 50–100% yield.[24]

A method for dehydrohalogenation in the two-phase catalytic system aqueous NaOH–heptane or methylene chloride using tetrabutylammonium hydrogen sulphate as the phase transfer catalyst has been developed in recent years. The reaction proceeds with an almost quantitative yield for the lowest members of the series, but, for compounds containing long aliphatic chains, the yields are sharply reduced owing to the poor solubility of the compounds.[25]

In view of the low solubility of higher alkyl halides and alkali metal salts of acetylene in liquid ammonia, the lithio-derivatives of terminal alkynes are alkylated in dipolar aprotic solvents: DMSO,[26] HMP,[27] and dimethylformamide (DMF)[28] and also in mixtures of these solvents in THF.[29,30] The yields of alkyl acetylenes increase when a complex of lithium acetylide and ethylenediamine (EDA) is used:[17,31]

$$EDA\cdot LiC{\equiv}CH + RX \rightarrow RC{\equiv}CH + LiX + EDA.$$

However, even in this case the yield of reaction products depends very greatly on the concentrations of the reactants and the order in which the reactants are mixed.[31]

In order to obtain higher acetylenic alcohols from alkylacetylenes, hydroxyalkyl halides with a protected alcohol group are used as alkylating agents.[32] HMP is the most suitable solvent for such reactions, because the yields of disubstituted acetylenes reach 60–80%.[33] The replacement of chlorine by bromine in tetrahydropyranyl (THP) ethers increases the yield by 10–15%. Unsubstituted ω-bromo-1-alkanols (V) or terminal acetylenic alcohols (VI) can also be used successfully for the syntheis of hydroxyalkylacetylenes:[34–36]

$$\left.\begin{array}{l} R{-}C{\equiv}CH + Br(CH_2)_nOH \\ \quad\quad (V) \\ H{-}C{\equiv}C(CH_2)_nOH \\ \quad\quad (VI) \end{array}\right| \xrightarrow[2)\ RHal]{1)\ LiNH_2/NH_3} R{-}C{\equiv}C(CH_2)_nOH.$$

In the latter case a mixture of a disubstituted acetylene and an ether—the *C*- and *O*-alkylation products respectively—is formed.[37] The fraction of the *C*-alkylation product can be increased sharply by carrying out the reaction in dipolar aprotic solvents,[38] in which there is a sharp increase of the nucleophilic reactivity of the carbanions. The yields of disubstituted acetylenes fall sharply to 28–33% when liquid ammonia, THF, and DMF are used as solvents owing to the poor solubility of the initial reactants.[1,39–41] Best results can be achieved by using DMSO[26,42] and the complex with EDA:[43]

$$HC{\equiv}CLi\cdot EDA + Br(CH_2)_8OH \xrightarrow{DMSO} HC{\equiv}C(CH_2)_8OH.$$

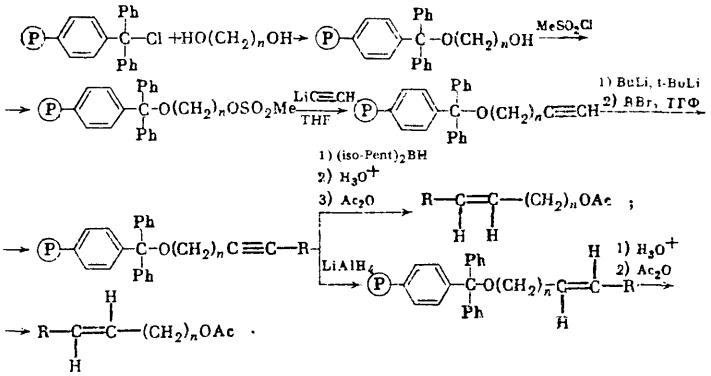
The tosylates [toluene-*p*-sulphonates] or brosylates [*p*-bromobenzenesulphonates] of the corresponding acetals can be used as alkylating agents, which makes it easier to carry out the reaction in liquid ammonia, because arenesulphonate esters are readily soluble in this solvent and are fairly resistant to ammonolysis:[44]

$$R{-}C{\equiv}C{-}Na + Ts(CH_2)_5CH(OMe_3)_2 \rightarrow \underset{(VII)}{R{-}C{\equiv}C(CH_2)_5CH(OMe_3)_2}.$$

However, the yields of the acetals (VII) fall sharply to 2–10% on passing to higher acetylenes or when higher alkyl bromides are used in this reaction.[45]

Acetylenic alcohols are converted into olefinic alcohols with the *cis*-configuration of the double bond by partial hydrogenation over the Lindlar catalyst. The reaction proceeds with a high overall yield. It is best to employ petroleum ether as the solvent.[46] On hydrogenation at 20 °C, the admixture of the *trans*-isomer is 1.5–3%, while on raising the temperature its content increases.[47] At low temperatures (between −10° and −30 °C) the degree of selectivity is higher and the admixture of the *trans*-isomer does not exceed 0.5%.[1] Other catalysts have also been used, namely $Pd/BaSO_4$,[35,48] nickel catalysts,[43] and others,[49] but they are less stereoselective. The degree of stereoselectivity is 98% in the hydrogenation by diisopentylborane with subsequent treatment by a carboxylic acid.[50] This method requires the use of a freshly prepared diisopentylborane, since otherwise the yields of the *cis*-isomer fall to 5%.[1]

The corresponding *trans*-isomer is obtained by reducing the alkyne with metallic sodium or lithium in liquid ammonia,[51] but the initial alkyne then remains in the reaction mixture, which is due to the limited solubility of higher acetylenic compounds in ammonia. The reaction proceeds with rigorous stereospecificity and an admixture of the *cis*-isomer is not detected.[52] The triple bond is reduced by lithium tetrahydroaluminate to a double bond with the *trans*-configuration in a high yield.[53] The reduction of alkynes by lithium tetrahydroaluminate in the presence of titanium tetrachloride leads to a mixture of isomers whose proportions depend on the temperature, the fraction of the *trans*-isomer diminishing as the temperature is reduced.[54] A method of synthesis of the *trans*-isomers of attractants on a polymeric support, which blocks one of the alcoholic groups of the initial diol or the alcohol group of the halogenoalcohol, has been developed. The polymer can be employed repeatedly, avoiding thereby laborious isolation processes. It has been established that the triple bond is not reduced by sodium in liquid ammonia on a polymeric support. In order to obtain the *cis*-isomer, diisopentylborane has been used as the reducing agent:[55–57]




*cis*-Dodec-8-enyl acetate, the pheromone of the oriental and common fruit moths (*Grapholitha molesta and Cydia molesta*), has been synthesised by a modification of the scheme described above:

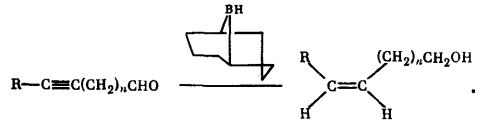
$$CH_3(CH_2)_2C{\equiv}CH + I(CH_2)_6Cl \rightarrow \underset{(VIII)}{CH_3(CH_2)_2C{\equiv}C(CH_2)_6Cl} \xrightarrow{NaCN} \underset{(IX)}{CH_3(CH_2)_2C{\equiv}C(CH_2)_6CN} \rightarrow \underset{(X)}{CH_3(CH_2)_2C{\equiv}C(CH_2)_6COOH} \rightarrow$$

$$\rightarrow CH_3(CH_2)_2C{\equiv}C(CH_2)_6CH_2OH \xrightarrow[2)Ac_2O]{1)H_2/Pd/CaCO_3} \underset{(XI)}{CH_3(CH_2)_2C(H){=}C(H)(CH_2)_7OAc}.$$

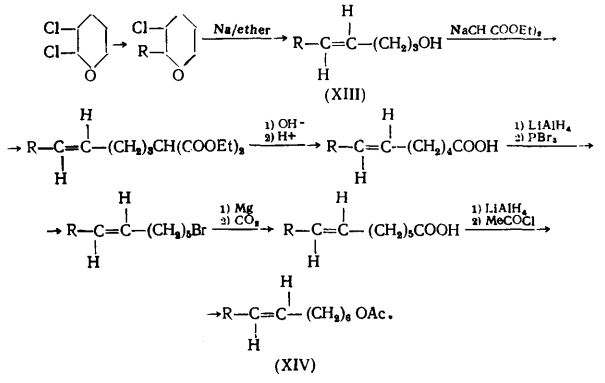
The lithium salt of pent-1-yne is alkylated by 1-chloro-6-iodohexane and the resulting chloroacetylene (VIII) is converted via the nitrile (IX) into the acid (X). Hydrogenation over the Lindlar catalyst with subsequent reduction of the carbonyl group and acetylation affords 46% of *cis*-dodec-8-enyl acetate (XI).[50,58] Sodium acetylides have been alkylated by chloro- and bromo-alkanes in DMSO [59] or by esters of carboxylic ω-chloroacids under the same conditions,[60] which led to the corresponding acid (XII) in 70% yield:

$$Cl(CH_2)_nCOOR + NaC{\equiv}CR' \xrightarrow{DMSO} R'{-}C{\equiv}C(CH_2)_nCOOR.$$

1-Alkenols, the active components of sex pheromones, are obtained by reducing acetylenic aldehydes by complex alkali metal hydrides with subsequent partial hydrogenation of the triple bond over the Lindlar catalyst.[60,61] Together with the *cis*-isomer, one then obtains up to 10% of the *trans*-isomer. A method has been developed for the synthesis of *cis*-alkenols in a high yield with the aid of 9-borabicyclo-[3.3.1]nonane—an effective reductant for carbonyl compounds, capable of simultaneous stereoselective reduction of the triple bond to the double bond having the *cis*-configuration:[62]



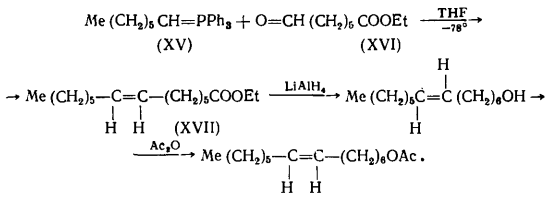
The stereoselective method of synthesis of *trans*-acetates involves the opening of the ring of 2-butyl-2-chlorotetrahydropyran with sodium in ether to form *trans*-4-non-4-en-1-ol (XIII); the chain is subsequently lengthened with the aid of diethyl malonate. The content of the *cis*-isomer is 1.3%.[63] The method has been used to synthesise *trans*-dodec-7-en-1-yl acetate (XIV):



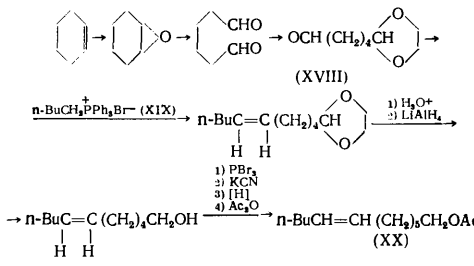
(XIV)

However, the yield of the acetate (XIV) was only 10% and the attractant obtained showed only a low activity in biological tests, evidently owing to the presence of impurities.

Numerous *cis*-mono-olefinic alcohols and their acetates have been synthesised by the Wittig reaction. The usual version of this process, involving the interaction of alkylidenetriphenylphosphoranes with carbonyl compounds, makes it possible to obtain olefins as mixtures of the *cis*- and *trans*-isomers. The high stereospecificity of this reaction, carried out in order to obtain the *cis*-isomer, is achieved using aliphatic phosphoranes and aliphatic aldehydes in non-polar solvents in the absence of lithium salts[64] and in dipolar aprotic solvents.[65–68] The formation of phosphorus ylides from the corresponding phosphonium salts by treatment with an alkali metal bis(trimethylsilyl)amide followed by subsequent interaction with aldehydes leads to *cis*-alkenes with 98% stereochemical purity.[69] This method has been used to synthesise attractants containing one unsaturated bond—*cis*-dodec-7- and *cis*-dodec-9-enyl acetates, *cis*-tetradec-7-enyl acetates, and others.[69–72] For example, the condensation of the ylide (XV) with the aldehyde (XVI) in THF at −78 °C leads to the unsaturated ester (XVII) with the ratio *cis* : *trans* = 98 : 2:[72]

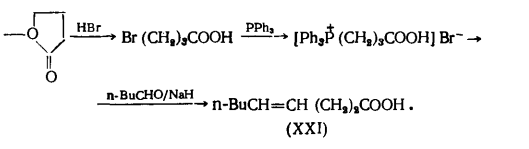


The geometrical isomers of dodec-7-en-1-yl acetate (XX) are the pheromones of the cabbage moth *Trichoplusia ni* and the leafroller *Argyroploce leucotreta*. These isomers were synthesised in cyclohexene in 27% yield. 6-Ethylenedioxy-1-hexanal (XVIII) was condensed with the phosphorane obtained from compound (XXIX):

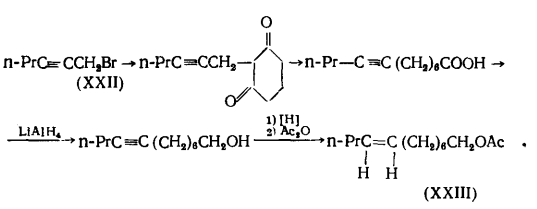


The mixture of the *cis*- and *trans*-isomers was separated chromatographically on silica gel impregnated with silver nitrate.[73]

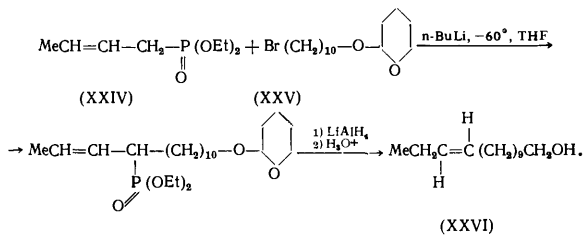
The yields and ratios of the isomers in the Wittig reaction differed depending on the nature of the solvent; thus the yield of non-4-enoic acid (XXI) was 46% in DMSO (with a ratio of the *cis*- and *trans*-isomers of 86 : 14), while in HMP the yield was 21% (91 : 9):[74]



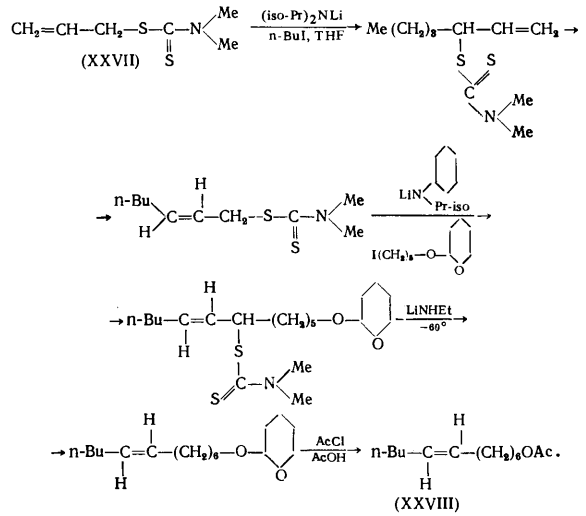
The highest stereospecificity has been observed in DMSO, DMSO/THF, DMF, or acetonitrile, where the fraction of the *cis*-isomer exceeds 90%.[75] *cis*-Dodec-8-enyl acetate (XXIII) has been obtained from cyclohexane-1,3-dione and the bromide (XXII):[76]



Alkylation of the lithio-derivatives of the γ-allylphosphonates (XXIV) in the α-position by various ω-substituted alkyl halides, for example, compound (XXV), with subsequent reduction by $LiAlH_4$ leads exclusively to the *trans*-isomer (XXVI):[77]

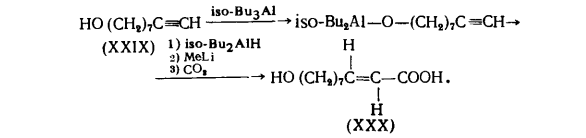


The stereoselective synthesis of *trans*-dodec-7-enyl acetate (XXVIII) has been achieved with the aid of the 3,3-sigmatropic rearrangement of the product of the alkylation of S-allyldithiocarbamate (XXVII):[78]

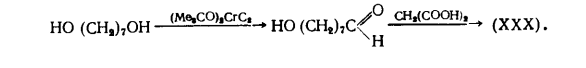


Mixed Kolbe electrolysis of carboxylic acid salts has also been used to obtain the acetate (XXVIII), but large amounts of dimerisation, transesterification, and disproportionation side products are formed.[74]

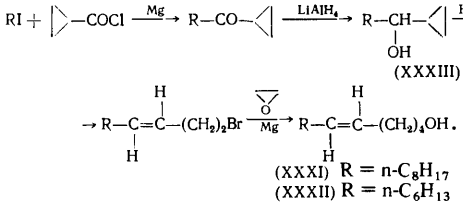
*trans*-10-Hydroxydec-2-enoic acid (XXX) is a component of royal jelly and a bee pheromone. It is synthesised from non-8-ynol (XXIX):[79]



The hydroxy-group in the nonynol (XXIX) is protected by introducing the diisobutylaluminium residue, after which the reaction mixture is treated with diisobutylaluminium hydride. The vinylalane formed is treated with methyllithium and subsequent carboxylation leads to the acid (XXX). The yield of 80% and the method is vigorously stereospecific. A simpler method of synthesis of the acid (XXX) with a smaller number of stages from readily available starting materials, involving the condensation of malonic acid with 8-hydroxyoctanal has been proposed:[80]



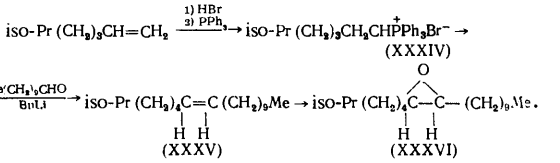
An interesting stereoselective synthesis of unsaturated $C_{12}$–$C_{15}$ alcohols and their acetates and epoxides has been achieved. Among them *trans*-tetradec-5-enol (XXXI) is a "pheromone simulator" (it stimulates the action of the natural pheromone) of the emarginate-winged moth *Pyncho pocha*, while *trans*-dodec-5-enol (XXXII) is the pheromone of the cereal fly *Tricimba cinctra*.[81] A characteristic feature of this method consists in the fact that the ethylenic bond in the final compound is formed on opening of the cyclopropane ring present in the initial carbinol (XXX):



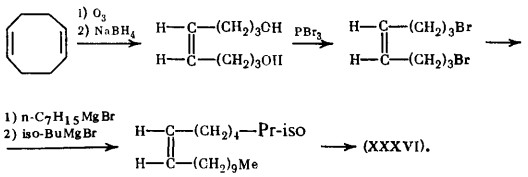
## II. DISPARLURE

An epoxide acting as a pheromone has been discovered hitherto only in the gypsy moth *Porthetria dispar* and has the structure of *cis*-7,8-epoxy-2-methyloctadecane—disparlure (XXXVI).[82] Biological tests of the enantiomers of compound (XXXVI) showed that the natural pheromone is a *cis*-(+)-isomer while the *trans*-isomer (XXXVII) and the *cis*-(−)-isomer are inactive.[83] These data indicate the chiral character of the receptor system of the gypsy moth.[84,85]

The racemic *cis*-disparlure has been synthesised in different ways. Condensation of the phosphonium salt (XXXIV) with 1-undecanal in DMSO in the presence of butyl-lithium in accordance with the Wittig reaction afforded the olefin (XXXV) with a ratio of the *cis*- and *trans*-isomers of 88 : 12.[82] The same reaction in HMP led to an isomer ratio of 96 : 6.[86] By reducing the reaction temperature to −78, it was possible to obtain the olefin (XXXV) and from the latter the epoxide (XXXVI) in 75% yield, the content of the *trans*-isomer not exceeding 2%:[87]

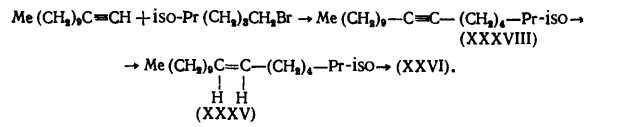


Racemic disparlure has been synthesised from cyclo-octadiene. The necessary *cis*-geometry of the double bond is determined by the stereochemistry of the initial cyclo-octadiene. Selective ozonolysis with subsequent treatment of the ozonide with sodium tetrahydroborate, the Grignard reaction, and epoxidation lead to disparlue in 25% yield:[88]



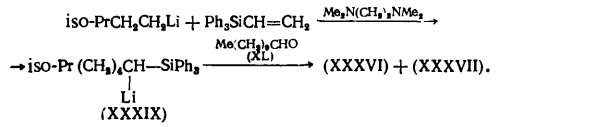
Disparlure has also been obtained from linear butadiene and isoprene oligomers by reaction with methyl acrylate. The synthesis is based on the Wittig reaction, which gives rise to an 85–95% yield and a ratio of the *cis*- and *trans*-isomers of the product of 3 : 1.[89]

The key stage in another method of synthesis of the racemic epoxide (XXXVI) involves the formation of the cisoid double bond, which is achieved by the controlled hydrogenation of 2-methyloctadec-7-yne (XXXVIII):[90–93]

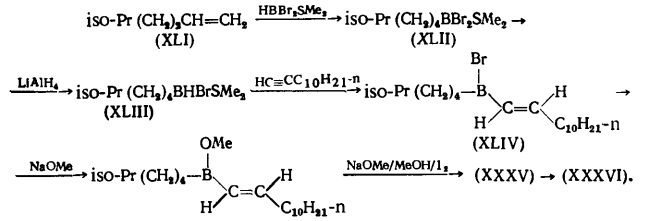


A method for the alkylation of the salts of aceylenes in HMP with a 35–45% yield of dialkylacetylenes has been developed for a large series of compounds.[93] Hydrogenation of the alkyne (XXXVIII) over the Lindlar catalyst leads to the *cis*-olefin, while reduction with sodium in liquid ammonia affords the *trans*-isomer. The purity of the *cis*-olefins obtained was 99%.

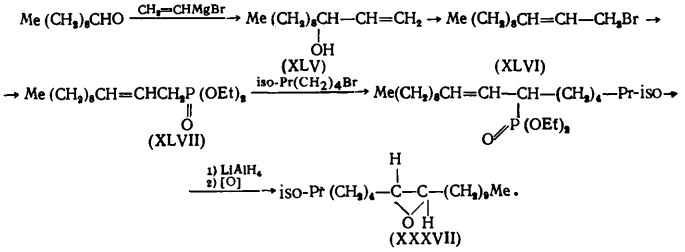
Condensation of 6-methyl-1-triphenylsilylheptyl-lithium (XXXIX) and 1-undecanal (XL) followed by epoxidation yielded a 1 : 1 mixture of the *cis*- and *trans*-isomers of disparlure:[94]



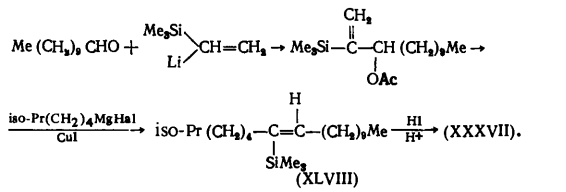
A convenient stereospecific synthesis of racemic disparlure using organoboranes has been proposed.[25] 5-Methylhex-1-ene (XLI) was converted into dibromo-5-methylborane-dimethyl sulphide (XLII), which was treated with lithium tetrahydroaluminate and the resulting bromoborane (XLIII) was added to dodec-1-yne:



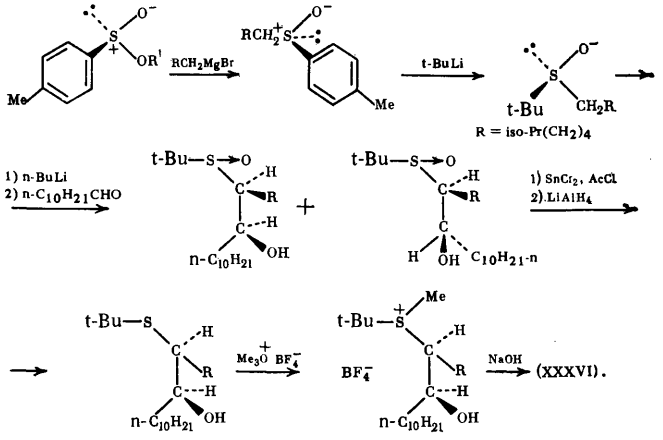
Treatment of the organoborane compound (XLIV) with sodium methoxide followed by iodination in the presence of sodium methoxide in methanol leads to the *cis*-isomer of the olefin (XXXV) in 55% yield (the isomeric purity is more than 99%). Disparlure was obtained by oxidation with *m*-chloroperbenzoic acid. In order to test the pheromone-inhibitor, the racemic *trans*-isomer of disparlure (XXXVII) was synthesised.[96] Nonylvinylmethanol (XLV), obtained by the reaction of 1-decanal with vinylmagnesium bromide, was treated with concentrated HBr. The resulting bromide (XLVI) was heated with triethyl phosphite and the corresponding phosphonate (XLVII) was alkylated with 5-methylhexyl bromide. The subsequent reduction with lithium tetrahydroaluminate and oxidation with *m*-chloroperbenzoic acid lead to the *trans*-isomer (XXXVII) in 81% yield:



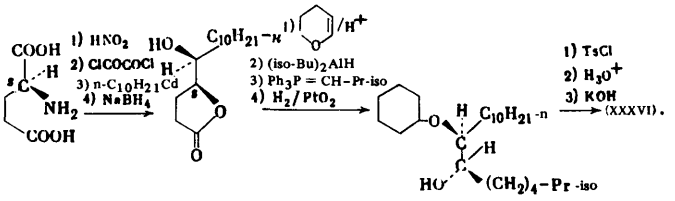
The *trans*-isomer (XXXVII) has been obtained in 65% yield by the protodesilylation of the corresponding vinylsilane (XLVIII):[97]



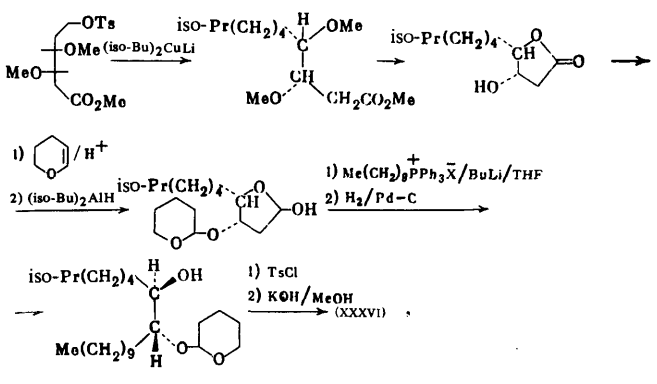
A six-stage synthesis of the optically active *cis*-(+)-disparlure in 15% yield has been proposed:[98]



An elegant synthesis of *cis*-(+)-disparlure has been achieved via (*S*)-(+)-glutamic acid:[99]



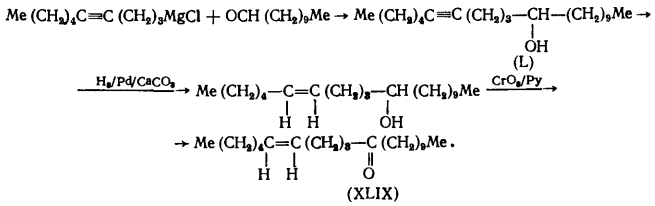
The same compound has been obtained with a high optical purity (98%) from (L)-(+)-tartaric acid:[100]



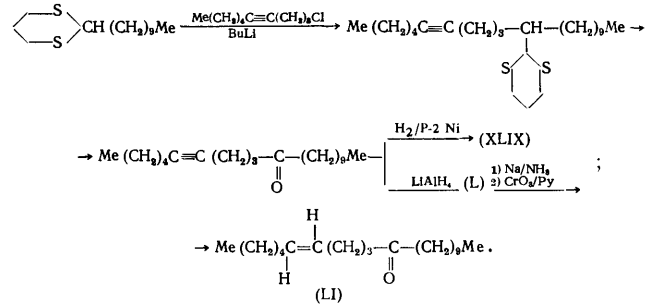
## III. UNSATURATED KETONES

Ketones are extremely rare among the known Lepidoptera pheromones. *cis*-Heneicos-6-en-11-one (XLIX) has been identified in *Orgyia pseudotsugata*.[101] It was

synthesised by the Grignard reaction from 1-undecanal and 1-chlorododec-4-yne; hydrogenation of the triple bond in the resulting alcohol (L) and oxidation of the alcoholic group lead to the pheromone (XLIX) with an admixture of 4% of the *trans*-isomer:[1]

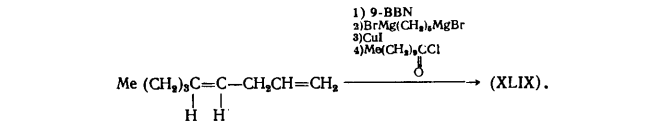


The *trans*-isomer (LI) was obtained in accordance with the scheme presented below:[101]

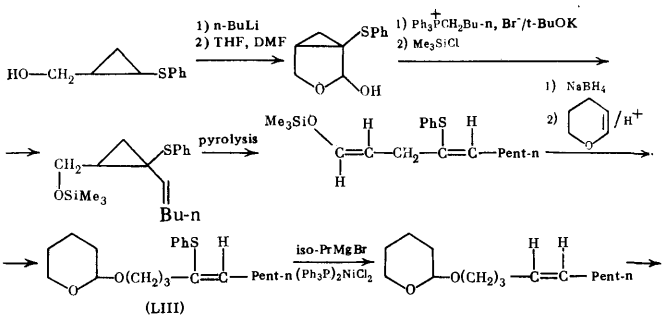


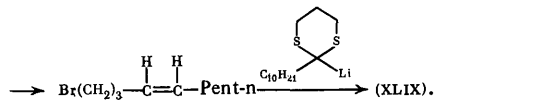
Alkylation of the lithium salt of 2-n-decyl-1,3-dithiane with subsequent hydrogenation results in the formation of the ketone (LII) whose carbonyl group is reduced by lithium tetrahydroaluminate and the triple bond is reduced to the *trans*-olefin with sodium in liquid ammonia. Catalytic hydrogenation over a nickel catalyst in the presence of EDTA affords compound (XLIX) (stereochemical purity 97%).[101]

The conversion of trialkylboranes into alkylmagnesium bromides has also been used to synthesise compound (XLIX).[102] *cis*-Deca-1,4-diene is hydroborated with 9-borabicyclononane (9-BBN), 1,5-pentamethylenedi(magnesium bromide) is added and the dec-4-enyl-9-BBN-magnesium bromide formed *in situ* is treated with copper(II) iodide and then with undecanoyl chloride, as a result of which the ketone (XLIX) is obtained in 78% yield:

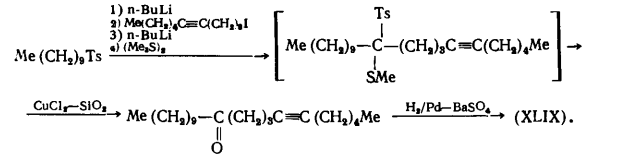


In the presence of bis(triphenylphosphine)nickel chloride, isopropylmagnesium bromide reduces the vinyl sulphide (LIII) stereospecifically to the corresponding olefin. This process has been used as the key stage in the synthesis of the unsaturated ketone (LXIX):[103]

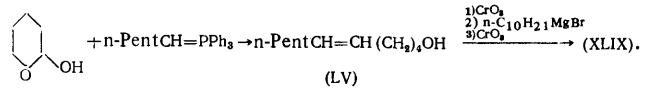




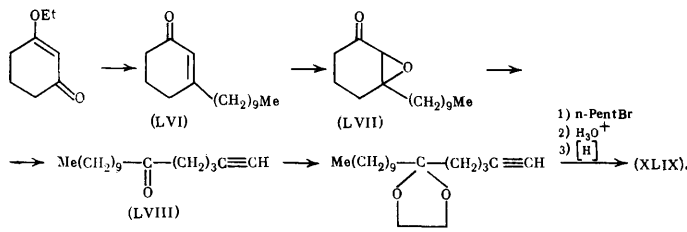
An alternative method of synthesis of the pheromone (LXIX), based on the preparation of dialkylacetylene (LIV) with subsequent Lindlar reduction,[104] is presented below:



The interaction of 2-hydroxypyran with hexylidenetriphenylphosphorane leads to undec-5-enol (LV) with a very high degree of geometrical purity. Oxidation of the resulting alcohol with chromium trioxide to the corresponding aldehyde, subsequent interaction with n-decylmagnesium bromide, and repeated oxidation afford compound (XLIX):[105]

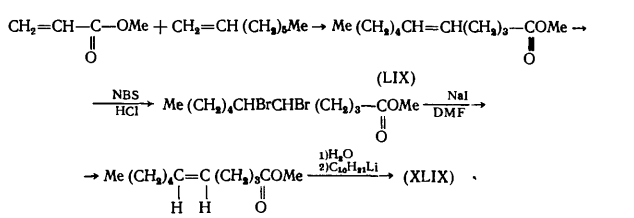


The pheromone (XLIX) has been obtained in a low yield from dihydroresorcinol in accordance with the scheme presented below:

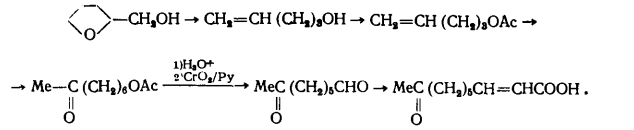


3-Ethoxy-2-cyclohexenone was converted by alkylation and hydrolysis into the αβ-unsaturated ketone (LVI), whose oxidation afforded the αβ-epoxyketone (LVII). The acetylenic ketone (LVIII) was obtained from the epoxide and then alkylated and hydrogenated over the Lindlar catalyst.[76] *cis*-Undec-5-en-2-one, an intermediate in the synthesis of pheromones, was synthesised by an analogous method.[106]

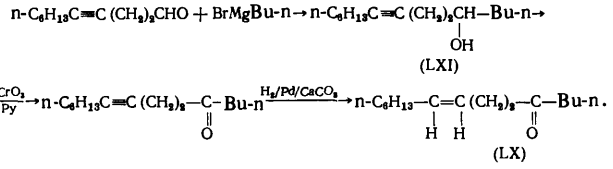
The interaction of methyl acrylate with 1-olefins in the presence of the eutectic mixture of aluminium, potassium, and sodium chlorides results in the formation of the unsaturated ester (LIX) in 40% yield, from which the pheromone (XLIX) was obtained:[107]



A simple and easy method of synthesis from tetrahydrofuryl alcohol of the intermediate for the synthesis of pheromones has been proposed:[108]



The pheromone of the peach moth *Carposina niponensis* consists of two components: the major component *cis*-eicos-7-en-11-one (LX) and the minor component *cis*- or *trans*-nonadec-7-en-11-one.[109] The key compound, 1-alkylundec-4-yn-1-ol (LXI), was obtained by treating the corresponding aldehyde[109] or nitrile[110,111] with a Grignard reagent:

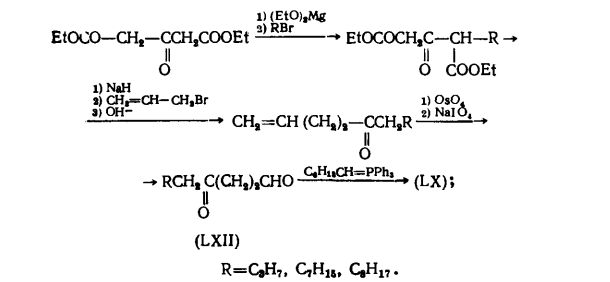


(LXI)



(LX)

Regioselective two-stage alkylation of acetonedicarboxylate ester with subsequent oxidation to the γ-ketoaldehyde (LXII), which was then made to undergo the Wittig reaction, has also been used to obtain compound (LX).[112] The reaction of the ketoaldehyde (LXII) with heptylidenetriphenylphosphorane at a low temperature leads to the *cis*-olefin (LX) in 20% yield.[113] In the presence of crown-ether (12-crown-4), the same reaction proceeds with a yield of 64%[112] and the content of the *cis*-isomer in the ketone (LX) exceeds 90%:



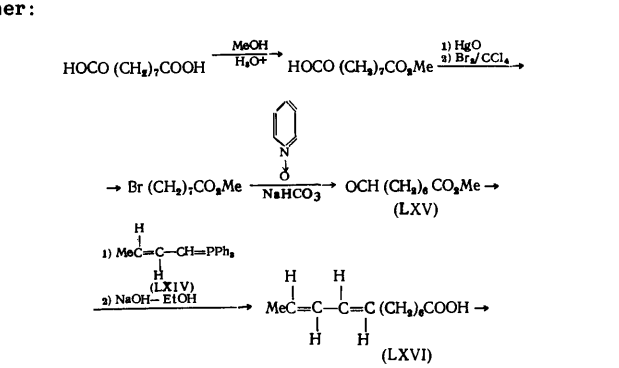
(LXII)

R=$C_5H_7$, $C_7H_{15}$, $C_9H_{17}$.

## IV. CONJUGATED DIENE ALCOHOLS, ACETATES, AND ALDEHYDES

Among the pheromones of the Lepidoptera, numerous compounds containing conjugated double bonds are known.[1,4,5] The methods of synthesis of compounds of this type discussed below illustrate the procedures used to obtain conjugated systems with the *trans*-configuration.

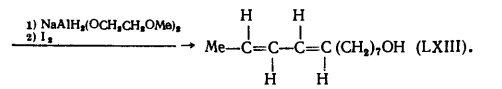
The pheromone of the lesser apple-worm *Laspeyresia pomonella*, *trans,trans*-dodeca-8,10-dien-1-ol (LXIII), was first obtained[114] by means of the Wittig reaction from *trans*-butenylidenetriphenylphosphorane (LXIV) and methyl 8-oxo-octanoate (LXV) in DMF in the presence of sodium methoxide. The acid (LXVI) has also been obtained as a mixture of 75% of the 8-*trans*,10-*trans*-isomer and 25% of the 8-*cis*,10-*trans*-isomer:



(LXV)

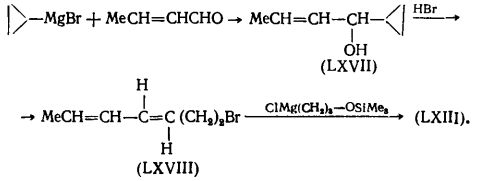
(LXIV)

(LXVI)



After reduction and isomerisation on treatment with iodine, the pure *trans*-isomer (LXIII) was obtained but in a very low yield. A high yield of the isomeric mixture consisting of 45% of the 8-*trans*,10-*trans*-isomer, 39% of the 8-*cis*,10-*trans*-isomer, and 16% of the 8-*trans*- and 8-*cis*,10-*cis*-isomers has been achieved by the reaction of the trans-ylide (LXIV) with ethyl 8-oxo-octanoate in the presence of lithium bromide.[1] The ratio of the isomers in the absence of lithium bromide is virtually the same as under the conditions of the normal Wittig reaction.[5,115,116] If tetrahydropyranyloxyheptyl bromide is converted into the triphenylphosphonium salt and the Wittig reaction with *trans*-but-2-enal is carried out, the yield is only 10% and the product (LXIII) consists of a mixture of 77% of the 8-*cis*,10-*trans*-isomer, 20% of the 8-*trans*,-10-*trans*-isomer, and 3% of a mixture of the 8-*trans*,10-*cis*- and 8-*cis*,10-*cis*-isomers.[115]

A higher stereoselectivity of the process was achieved on opening the ring of the secondary alcohol cyclopropylpropenylmethanol (LXVII) with hydrobromic acid, which leads to a mixture of 90% of 3-*trans*,5-*trans*- and 10% of 3-*cis*,5-*trans*-heptadienyl bromides (LXVIII). The Grignard reaction in the presence of $Li_2CuCl_4$ and subsequent hydrolysis lead to 79% of the alcohol (LXIII) containing 9% of the 8-*cis*,10-*trans*-isomer and 12% of the 8-*cis*(*trans*),10-*cis*-isomer:



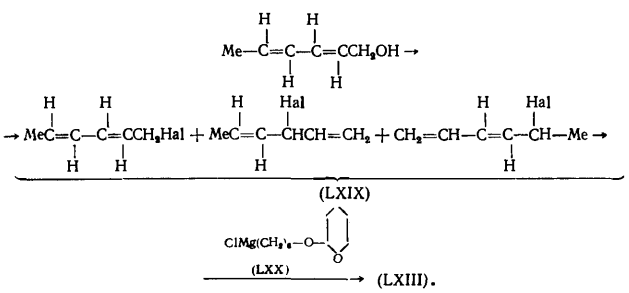
(LXVII)



(LXVIII)

Recrystallisation of this mixture yielded the alcohol (LXIII) (with 99.5% purity).[117] In many studies *trans,trans*-dodecadodeca-8,10-dien-1-ol was obtained in a low yield and the reaction product contained also a whole series of other geometrical isomers, the stereospecificity of the reaction being unknown.[1]

The interaction of the allyl halides (LXIX) with Grignard reagents not containing double bonds, leading to a complex mixture of the geometrical isomers of the alcohol (LXIII), has been studied in detail.[118] The interaction of the isomeric mixture of the halides (LXIX) with the Grignard reagent (LXX) leads mainly to oct-2-ene and only trace amounts of a diene product:[119]

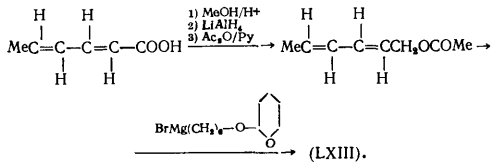


(LXIX)

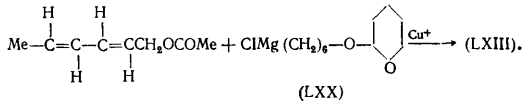
(LXX)

A number of attempts to convert sorbyl alcohol into the corresponding halide without an allylic rearrangement proved unsuccessful.[120,121] Using sorbyl bromide, obtained from sorbyl alcohol and phosphorus tribromide, various investigators were able to obtain 25–30% of the alcohol (LXIII) containing only 75% of the *trans,trans*-isomer.[122–124]

The interaction of sorbyl acetate with organomagnesium and organolithium reagents in the presence of univalent copper salts has been investigated.[125] The reaction is rigorously stereo- and regio-specific with formation of *trans,trans*-dodeca-8,10-dien-1-ol (99.7% stereochemical purity):[125,126]

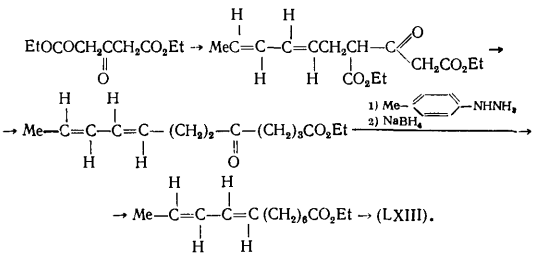


A single-stage synthesis of the dodecadienol (LXIII) from *trans,trans*-1-acetoxyhexa-2,4-diene and the Grignard reagent (LXX) has been achieved in the presence of a univalent copper salt:[127]

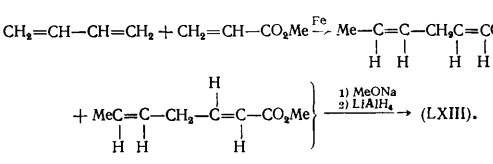


(LXX)

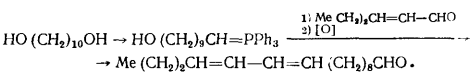
Using the selective alkylation of acetonedicarboxylate ester initially with sorbyl bromide and then with 3-bromopropionate and subsequent hydrolysis, decarboxylation, and reduction, the alcohol (LXIII) was synthesised in a fairly high yield:[128]



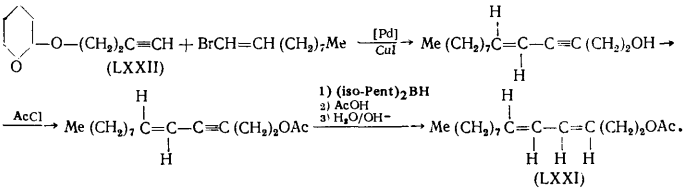
New possibilities for the synthesis of diene attractants appeared when the co-oligomerisation of 1,3-dienes with acrylates, catalysed by transition metals, was employed. The codimerisation of butadiene with methyl acrylate leads to a mixture of *cis,cis*- and *trans,cis*-hepta-2,5-dienoic acids. The isomerisation of this mixture by treatment with sodium ethoxide leads to a quantitative yield of *trans,trans*-hepta-3,5-dienoic acid, which is reduced to an alcohol:[129]



*trans,trans*-Hexadeca-10,12-dienal, the principal component of the pheromone of *Earias insulana*, has been obtained from 1,10-dihydroxydecane; the Wittig reaction, which leads to a mixture of the 10-*trans*,12-*trans*- and 10-*cis*,12-*trans*-isomers, was used as the key stage:[130]

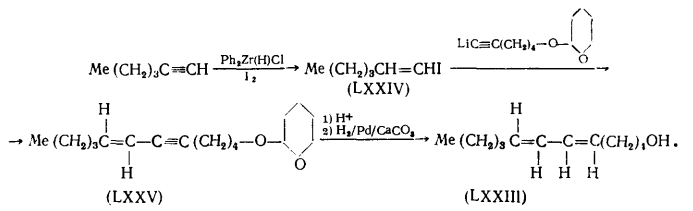


The application of metal complex catalysis makes it possible to obtain *trans,trans*-dienes with a high stereochemical purity. Thus *cis,trans*-tetradeca-3,5-dienyl acetate (LXXI), the pheromone of *Prionoxystus rebiniae*, has been obtained by the direct stereospecific cross-coupling of the ω-substituted alkyne (LXXII) with *cis*-1-bromodecene in the presence of tetrakis(triphenylphosphine)palladium and copper(I) iodide.[131] The stereospecificity of this reaction is greater than 97%. When it is carried out under phase transfer catalysis conditions, the yield of the pheromone (LXXI) is increased to 70%:



(LXXII) (LXXI)

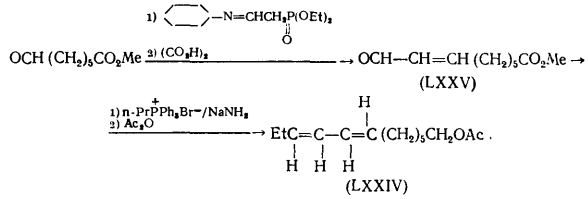
The cross-coupling of *trans*-1-iodohexene and tetrahydropyranyloxyhex-5-yne in the presence of bis(triphenylphosphine)palladium chloride was the key stage in the synthesis of *cis,trans*-dodeca-5,7-dien-1-ol (LXXII)—the pheromone of *Dendrolimus spectabilis*.[132] A regioselective synthesis of *trans*-1-iodoalk-1-enes (LXXIV) in the presence of a zirconium catalyst has been developed. The conjugated triple bond in compound (LXXV) gives rise to a mixture of 5% of the initial enyne (LXXV), 71% of the *cis,trans*-5,7-diene, and 24% of the monoene on hydrogenation over the Lindlar catalyst:



(LXXV) (LXXIII)

The stereochemically pure pheromone (LXXIII) was obtained by chromatographing the mixture on silica gel impregnated with silver nitrate. *cis,trans*-dodeca-5,7-dien-1-ol and the corresponding aldehyde are the components of the sex pheromone of *Malacosoma disstria*.[133] All four isomers of dodeca-5,7-dien-1-ol have been obtained stereoselectively by the Wittig condensation.[133]

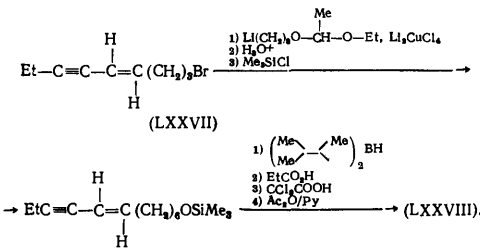
The αβ-unsaturated aldehyde (LXXV), obtained by the Horner reaction from the aldehyde (LXXVI) on treatment with didethyl 2-(cyclohexylimino)ethylphosphonate,[134] was used as the initial component for the synthesis of *trans,cis*-dodeca-7,9-dienyl acetate (LXXIV)—the pheromone of *Lobesia botrana*:[134,135,136]



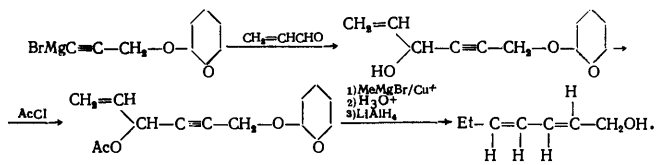
(LXXV) (LXXIV)

The interaction of the aldehyde (LXXV) with propylidenetriphenylphosphorane followed by its reduction with sodium dihydrobis(2-methoxyethoxy)aluminate leads to a 30% yield of a mixture of alcohols containing 70% of the required dodeca-7,9-dienol. This method is unsuitable for the synthesis of *trans,cis*-dodeca-7,9-dienyl acetate in any kind of large amount. The synthesis using a disubstituted acetylene proved promising for this purpose.[135] The condensation of the *trans*-conjugated enyne (LXXVII) with 3-(1-ethoxy)-ethoxypropyl-lithium and subsequent reduction lead to the

alcohol (LXXVIII) (purity 99%):[135]

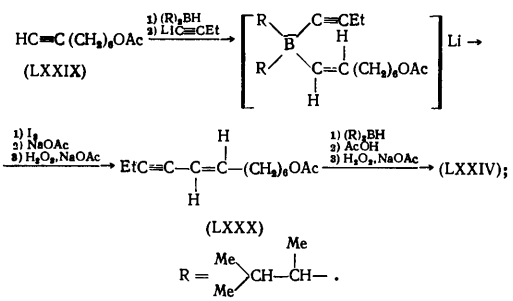


*trans,cis*-Hepta-2,4-dienol, which is a suitable intermediate for the synthesis of conjugated dienes, was obtained in accordance with the scheme:[137]



The *cis,cis*-isomer present (7%) is bound in a complex with tetracyanoethylene.

Another key intermediate for the synthesis of the *cis,trans*-conjugated system, namely *trans,dodec*-7-en-9-ynol (LXXX), was obtained in 20% yield by the hydroboration of octynyl acetate (LXXIX) followed by treatment with butynyl-lithium:[138,139]

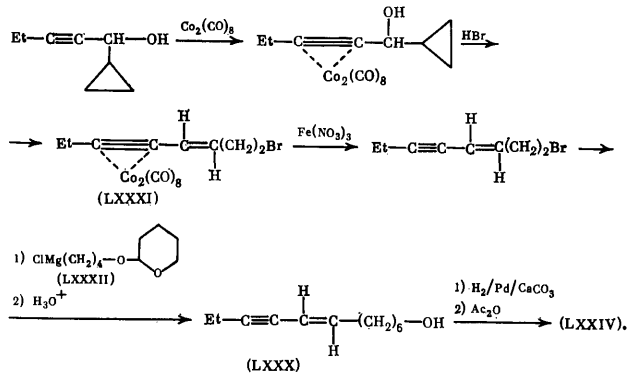


A modified method for the conversion of a *trans*-enyne into a *trans,cis*-diene, involving the selective reduction of the triple bond with zinc dust in aqueous propanol to a double bond with the *cis*-configuration, made it possible to obtain *trans,cis*-dodeca-7,9-dienyl acetate.[139,140]

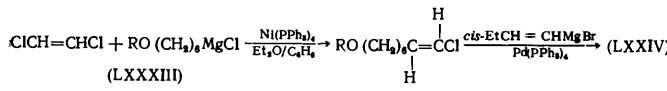
The triple bond of tetrahydropyranyloxy-*cis*-dodec-9-en-7-yne is reduced with diisopentylaluminium hydride.[141] However, owing to steric hindrance, *cis*-enynes react very slowly and after hydrolysis a mixture of the *cis*- and *trans*-isomers is obtained. Apparently the hydroalumination of the triple bond initially leads to the preferential formation of *trans*-vinylaluminium hydride, but, with increase of the duration of the reaction, the latter isomerises to the *cis*-isomer.

It was found that, when the ring of 1-cyclopropylpent-2-yn-1-ol is opened by hydrobromic acid, *cis*-1-bromooct-3-en-5-yne is formed as the main product (the *cis* : *trans* isomer ratio is 67 : 33).[142]

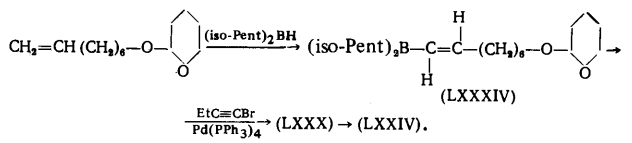
With increase of steric hindrance (as a result of the blocking of the triple bond by dicobalt octacarbonyl), the opening of the cyclopropane ring leads to the homoallyl bromide (LXXXI) with a purity of 99%.[143] When the bromide (I) reacts with the Grignard reagents (LXXXII) in the presence of copper(I), the *trans*-enyne (LXXX) is obtained in 80% yield (purity 96%). After the reduction of the triple bond over the Lindlar catalyst,[144] the yield of the dienol is 60% and the latter consists of 92% of the 7-*trans*,9-*cis*-isomer and 8% of the 7-*trans*,9-*trans*-isomer:



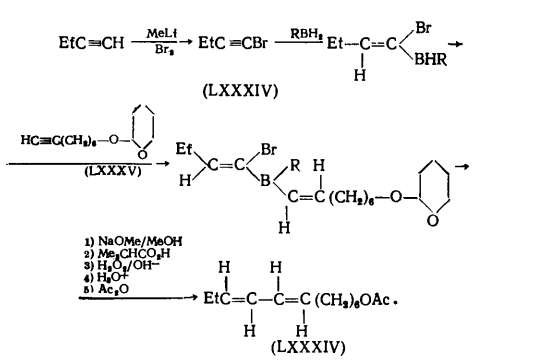
A new stereoselective synthesis of the pheromone (LXXIV) in 72% yield, based on the cross-coupling of *trans*-1,2-dichloroethylene with the Grignard reagent (LXXXIII) in the presence of tetrakis(triphenylphorphine)nickel, has been described recently. The reaction is accompanied by the almost complete (more than 99%) retention of the configuration at the double bond:[145]



The cross-coupling reaction of diisopentyl-*trans*-8-(2-tetrahydropyranoloxy)-en-1-octylborane (LXXXIV) with 1-bromobutyne in the presence of a palladium catalyst proceeds stereoselectively. Further acylation and hydroboration of the conjugated *trans*-enyne (LXXX) made it possible to obtain the alcohol (LXXIV) in 22% yield:[146]



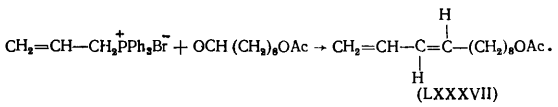
The stereoselective synthesis of conjugated *trans,trans*-systems was carried out by the hydroboration of the acetylenic derivatives (LXXXIV) and (LXXXV).[147] The purity of the *trans,trans*-7,9-diene (LXXXVI) is more than 99%:



*trans*-Dodeca-9,11-dienyl acetate (LXXXVII) is the main component of the pheromone of *Disparopsis castanea*—a pest on the cottonplant. This pheromone is a multicomponent

system containing a 1 : 4 mixture of the *cis*- and *trans*-dodeca-9,11-dienyl acetates, *trans*-dodec-9-enyl acetate, dodec-11-enyl acetate, and 1-dodecyl acetate.[148] The diene is the most active, but addition of the inactive dodec-11-enyl acetate to the diene (LXXXVII) (1 : 4) caused a sharp increase in the attracting effect. Each of these compounds separately inhibits the attraction by males, while dodec-9-enyl acetate influence the orientation of females. The role of 1-dodecyl acetate has not so far been elucidated.[148]

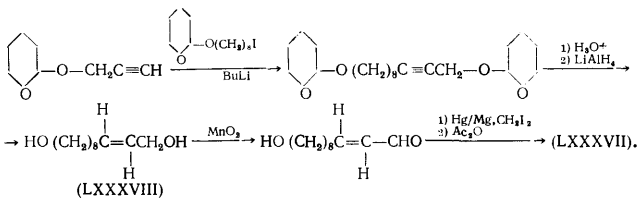
The Wittig reaction of triphenylphosphonium 2-propenylide with 9-oxononyl acetate in the presence of lithium bromide leads to 70% of a diene containing the *cis*- and *trans*-isomers of compound (LXXXVII) in proportions of 3 : 2:[148,149]



(LXXXVII)

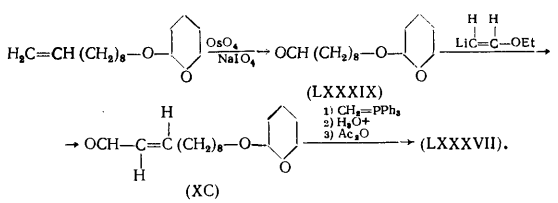
By varying the polarity of the solvent in the Wittig reaction, it is possible to achieve a 4 : 1 ratio of the *cis*- and *trans*-isomers, but a greater stereoselectivity cannot be achieved. The separation of the isomers is extremely difficult. However, by treating the products of the Wittig reaction with liquid sulphur dioxide and subsequent chromatography on Florisil, the product of the 1,4-cycloaddition of $SO_2$ was obtained. Its thermolysis takes place stereospecifically with formation of the diene (LXXXVII) whose stereochemical purity is in excess of 99%. The *cis*-isomer has been isolated in a satisfactory yield on treating the products of the Wittig reaction with tetracyanoethylene.[149,150]

Another stereospecific synthesis of the pheromone (LXXXVII) has been achieved, in which the starting compound was tetrahydropyranoloxypropyne. The key compound, the *trans*-olefin (LXXXVIII), was obtained by reducing the triple bond in a disubstituted acetylene with lithium tetrahydroaluminate:[151]



(LXXXVIII)

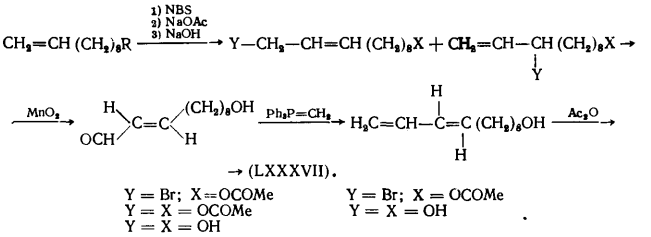
Oxidation of dec-9-enol with a mixture of osmium tetroxide and sodium metaperiodate leads to the aldehyde (LXXXIX), which is converted into the αβ-unsaturated aldehyde (XC) after condensation with β-ethoxyvinyl-lithium and subsequent rearrangement of the intermediate γ-ethoxyvinylmethanol. The aldehyde reacts with methylenetriphenylphosphorane to form the pheromone (LXXXVII)in 65% yield:[152,153]



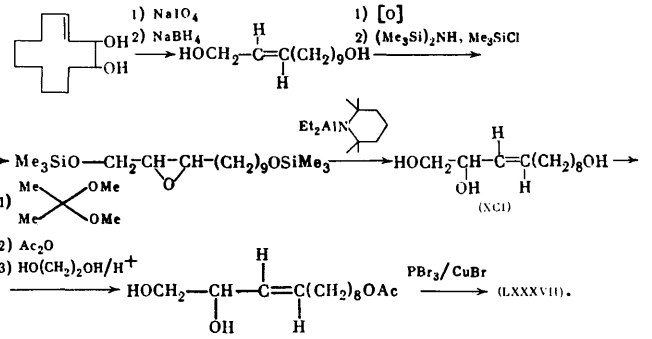
(LXXXIX)

(XC)

The *cis*–*trans* isomerisation of αβ-unsaturated aldehydes[154] makes it possible to obtain *trans*-11-hydroxyundec-2-enal[155] with a *cis* : *trans* ratio of 85 : 15; the acetate (LXXXVII) was synthesised from it by the Wittig reaction (purity 97%):

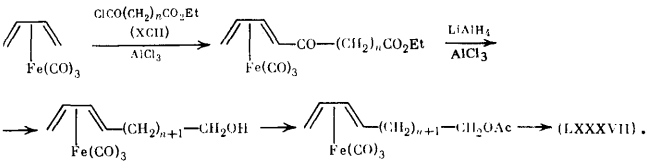


The regio- and stereo-specific opening of the oxiran ring by treatment with *N*-diethylalumino-2,2,6,6-tetramethylpiperidine has been used to convert the allyl alcohol (XCI) into the acetate (LXXXVII):[156]



The pheromone (LXXXVII) has also been synthesised by the stereospecific cross-coupling of *trans*-10-(2-tetrahydropyranyloxy)-1-decylborane and vinyl bromide in the presence of the palladium catalyst $Pd(PPh_3)_4$ in 54% yield.[146]

A novel method involving the use of the iron tricarbonyl protecting group, has been used to synthesise the pheromone (LXXXVII) with a high stereochemical purity (more than 99%). Butadieneiron tricarbonyl interacts with the acid chloride (XCII) under the conditions of the Friedel–Crafts reaction and subsequent reduction, acylation, and removal of the protecting group leads to compound (LXXXVII):[156]

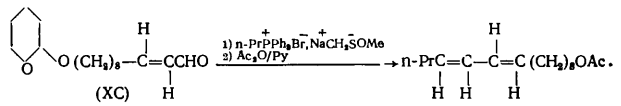


*cis*,*trans*-Tetradeca-9,11-dienyl acetate (XCIII) is the sex pheromone of the cotton pest *Spodoptera littoralis*.[148] The butterfly produces four compounds: tetradec-1-enyl acetate, *cis*,*trans*-tetradeca-9,11-dienyl acetate, *cis*-tetradec-9-enyl acetate, and *trans*-tetradec-11-enyl acetate.[10] Only the dienyl acetate has an attracting effect.[157] Tetradec-9-enyl acetate exhibits an inhibiting influence and the role of the other components has not been elucidated. Admixtures of the *cis*,*cis*- and *trans*,*cis*-isomers diminish the attracting effect.[157]

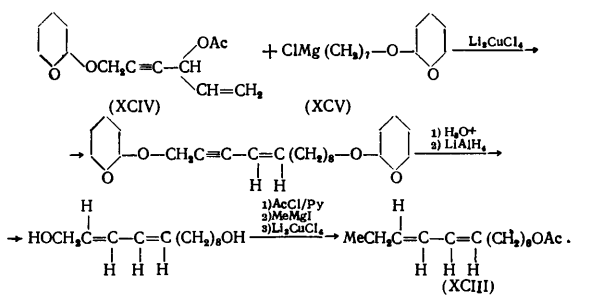
The same diene, namely *cis*,*trans*-tetradeca-9,11-dienyl acetate, forms part of the composition of the pheromone of *Spodoptera litura* in combination with *cis*,*trans*-tetradeca-9,12-dienyl acetate.[158] There are data showing that the mixture in proportions of 20 : 1 is active for *Spodoptera littoralis*.[148,157] There exist also directly opposed data

indicating that the 9-*cis*,12-*trans*-isomer inhibits the activity of the *cis*,*trans*-9,11-diene when present in proportions of 1 : 20 or 1 : 50.[159]

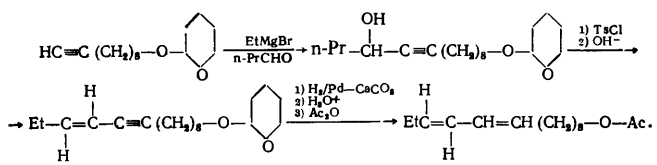
Compound (XCIII) has been synthesised from *trans*-pent-2-enyltriphenyl phosphonium bromide and 9-oxononyl acetate via the Wittig reaction, but the reaction is non-stereospecific.[148] It was later established that the ratio of the isomers in this reaction depends on solvent polarity: it is 40 : 60 in benzene, being reversed to 60 : 40 in DMSO.[160] The Wittig reaction of *trans*-pent-2-enal and 9-tetrahydropyranyloxynonylide in DMSO with subsequent acid hydrolysis and acetylation leads to a mixture of the 9-*cis*,11-*trans*- and 9-*trans*,11-*trans*-isomers in proportions of 80 : 20.[161] The interaction of *trans*-undec-2-enal with propylidenetriphenylphosphorane in THF in the presence of dimsylsodium and subsequent hydrolysis and acetylation make it possible to obtain the 9-*trans*,11-*cis*-isomer of the pheromone (XCIII) with a purity of 98%:[162]



The regioselective reaction of the substituted enyne (XCIV) with the Grignard reagent (XCV) in the presence of dilithium tetrachlorcuprate and subsequent partial diacetylation make it possible to obtain compound (XCIII) in a fairly high yield:[163]

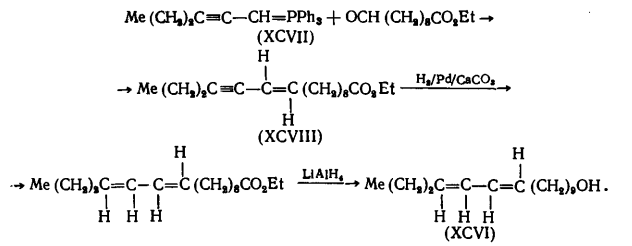


Another method, illustrated below, has also been used to synthesise compound (XCIII),[158,159] a mixture of the 9-*cis*,11-*trans*- and 9-*cis*,11-*cis*-isomers being obtained:

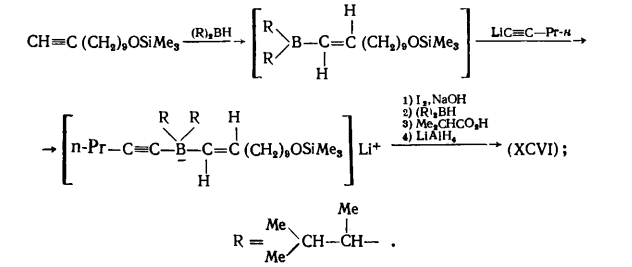


The attractant of the silkworm *Bombyx mori*, namely *trans*,*cis*-hexadeca-10,12-dienol (bombykol) (XCVI) was discovered by Butenand et al. in 1959.[164] It was assumed that this is the only pheromone of the butterfly, but subsequently data were obtained showing that there exist a further two components: hexadeca-10,12-dienal ("bombykal") and *trans*,*trans*-hexadeca-10,12-dienol.[165]

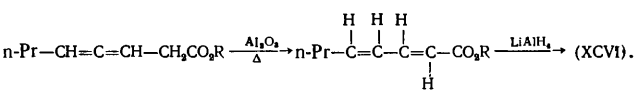
The pheromone (XCVI) has been obtained by the Wittig reaction involving the condensation of hex-2-ynylide (XCVII) with ethyl 10-oxodecenoate. The enyne product (XCVII) contained the *trans*- and *cis*-isomers in approximately equal amounts. The conjugated enyne (XCVIII) was hydrogenated over the Lindlar catalyst and the ester group was reduced with lithium tetrahydroaluminate to the alcoholic group:[164]



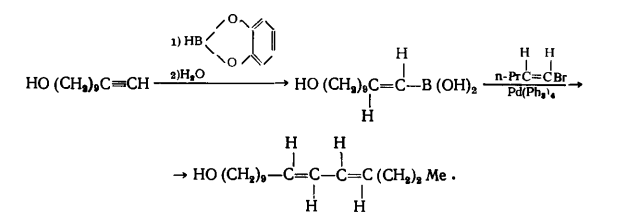
A method of synthesis in which the lithium salt of the pentyne was condensed with 1,2-epoxy-11-tetrahydropyranyloxyundecane to form an alcohol, the latter was converted into a toluene-*p*-sulphonate, and the conjugated enyne was obtained in the form of a mixture of the *trans*- and *cis*-isomers after splitting off the toluenesulphonic acid has also been used. The mixture was separated with the aid of a complex with urea and the *trans*-isomer was hydrogenated over the Lindlar catalyst. As already mentioned above, the process is relatively non-stereospecific and the yield of the desired product is low.[5] The hydroboration of the conjugated enyne system proceeds more stereospecifically. The scheme quoted below demonstrates the application of hydroboration to the synthesis of bombykol:[139]



Bombykol has also been obtained with the aid of cuprates[167] and a stereocontrolled rearrangement of a β-allene ester in the presence of alumina:[168]

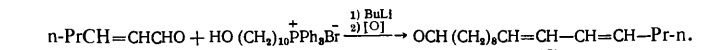


The reaction of alkenylboronic acid (XCIX) and a suitable alkenyl halide, catalysed by a palladium complex in the presence of a base, leads to *trans*,*trans*-dodeca-10,12-dien-1-ol in a high yield (66–91%) and a purity of 99%:[169]



*trans*,*trans*-Hexadeca-10,12-dienal (C), the main component of the sex pheromone of *Earias insulana*, has been obtained by a four-stage synthesis, in which the key stage is the Wittig reaction, leading to a mixture of the *trans*,*trans*- and

*cis,trans*-isomers of compound (C) in proportions of 1 : 4:[170]

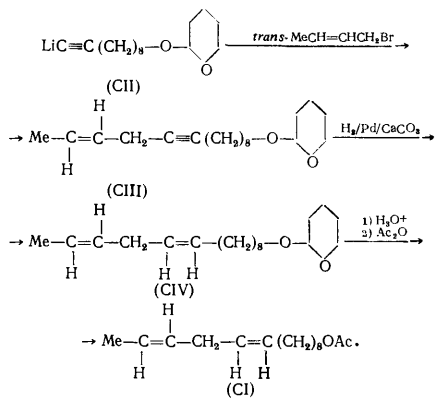


(C)

## V. NON-CONJUGATED DIENE ALCOHOLS AND ACETATES

Non-conjugated dienes have been identified in a large number of insects of the order Lepidoptera.[5] Thus, *cis,trans*-tetradeca-9,12-dienyl acetate (CI) proved to be the pheromone of *Plodia interpunctella* and *Cadra cautella*.[171, 172] In a mixture with *cis*-tetradec-9-enyl acetate, this diene proved to be the pheromone of *Spodoptera eridania*.[173] The same compound has been identified in *Anagasta kühniella*,[174] *Ephestia elutella*,[175] *Cadra figulitella*,[176] and *Spodoptera litura*.[177] The *cis,cis*-, *trans,cis*-, and *trans,trans*-isomers of the pheromone (CI) are inhibitors. *cis,trans*-Tetradeca-9,12-dienol is an inhibitor of the pheromone of *Plodia interpunctella*.[178] Data have been published showing that *cis,trans*-tetradeca-9,12-dienyl acetate and *cis*-tetradec-9-enyl acetate are inactive in relation to *Spodoptera exigua* either individual or when combined.[179]

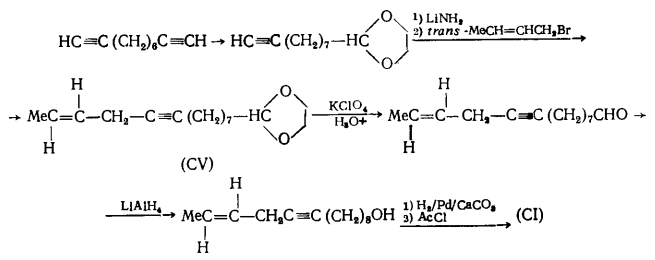
The *cis*,trans-1,4-diene system has been obtained in accordance with the scheme



(CII) (CIII) (CIV) (CI)

The interaction of the lithium salts of the acetylene (CII) with *trans*-1-bromobut-2-ene in dioxan leads to the enyne (CIII), whose partial reduction affords an 86% yield of the diene (CIV). The acetylation of the diene gives rise to the pheromone (CI). All the other isomers of tetradeca-9,12-dienyl acetate have been obtained in accordance with the same scheme.[174,180]

An analogous method is based on the use of deca-1,9-diyne and crotyl alcohol:[181]

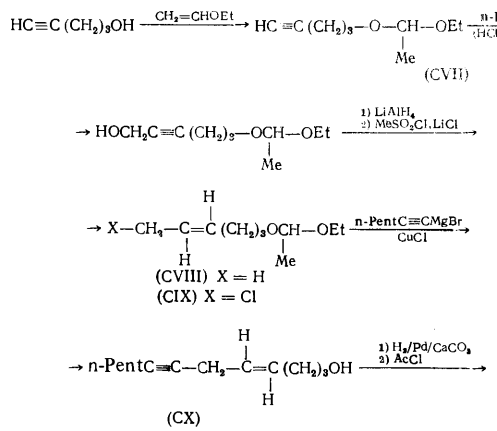


(CV)

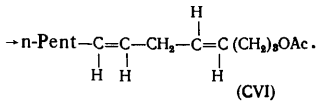
The enyne alcohol (CV) has been obtained in 29% yield by the reaction of the Grignard reagent derived from *trans*-1-bromobut-2-ene with the lithium salt of an ω-substituted non-1-yne in THF in the presence of CuCl and CuCN. The formation of the 1,4-enyne (CV) by the reaction of 1-alkynyllithium and *trans*-1-bromobut-2-ene in dioxan is none other than the reaction of a strong base with an allyl halide, which always leads to a complex mixture of products. The products of the allylic rearrangement and isomerisation (a conjugated enyne) are accompanied by the products of the deprotonation of the 1,4-enyne and of further alkylation.[182,183] It has been found that the reaction of 1-alkynylsodium with allyl halide in ammonia leads to mono-, di-, and tri-alkylated compounds.[183] For example, propynylsodium reacts with one equivalent of 1-chlorobut-2-ene in liquid ammonia to give a mixture of products: 40% of the monoalkyl derivative and 55% of the dialkyl derivative. 1,4-Enynes can be obtained by the reaction of alkylmagnesium halide with allyl halide in ether[184] or THF in the presence of CuCl as the catalyst.[182,185] In the absence of a copper (I) salt, the reaction proceeds very unsatisfactorily or not at all.[186] A version of this method, which involves the interaction of allyl halide and a terminal acetylene on treatment with an amine and catalytic amounts of a copper salt (the Cadiot-Chodkiewicz method), is not very convenient for the synthesis of 1,4-enynes, because the normal alkylation product and the isomeric products of the allyl rearrangement are obtained in equal amounts. In dipolar aprotic solvents the reaction proceeds with the allyl rearrangement. Thus, the reaction of heptynylcopper with 1-bromobut-2-ene in HMP leads to a mixture of undec-9-en-6-yne and the rearrangement product (8-methyldec-9-en-6-yne) in proportions of 3 : 1 and 76% yield.[187] The enynes are formed in the same proportions in the reactions of the *cis*- and *trans*-isomers of 1-chlorobut-2-ene with copper phenylacetylide. In an attempt to reduce to a minimum the product of the allyl rearrangement, the reaction has been carried out in the presence of CuCl, whereupon 9% of the allyl product is formed in THF.[184] In THF in the presence of CuCN, *trans*-1-chlorobut-2-ene yields 15% of the allyl product, while in the presence of $LiCuCl_2$ it amounted to only 4.4%.[185]

A mixture of 95% of *cis,trans*-tetradeca-9,12-dienyl acetate and 5% of the *trans,trans*-isomer has been obtained by the Wittig reaction from triphenylphosphonia-*trans*-pent-3-enylide and 9-acetoxy-1-nonanal in HMP[186] or in DMSO.[187] The 1,4-diene is oxidised in air at room temperature[185] and irradiation with ultraviolet light leads to a mixture of *cis,trans*-13-hydroperoxytetradeca-9,11-dienyl acetate and *trans,trans*-9-hydroperoxytetradeca-10,12-dienyl acetate.[188] In order to stabilise the pheromone, an antioxidant is added, namely *N*-octyl-*N'*-phenyl-1,4-phenylenediamine.[195]

*trans,cis*-Trideca-4,7-dienyl acetate (CVI) is the pheromone of *Phthorimaoea operculella*.[188] A second active component of the pheromone of this species has been identified—*trans*,-*cis,cis*-trideca-4,7,10-trienyl acetate.[189] The acetate (CVI) has been obtained in accordance with the scheme



(CVII) (CVIII) X = H (CIX) X = Cl (CX)



(CVI)

Pent-4-yn-1-ol is converted by the reaction with ethyl vinyl ether into the mixed acetal (CVII), which gives rise to the alcohol (CVIII) after treatment with n-butyl-lithium, reaction with paraformaldehyde, and reduction. The alcohol was converted into the chloride (CIX) by treatment with methanesulphonyl chloride in the presence of lithium chloride and collidine.[190] The allylic rearrangement is virtually ruled out under these conditions and the acid-sensitive acetal protecting group is unaffected. The reaction of allyl chloride (CIX) with 1-heptynylmagnesium bromide was carried out in the presence of catalytic amounts of copper monochloride. Hydrolysis with trichloroacetic acid in aqueous THF and low-temperature crystallisation of the product lead to a derivative of the enyne alcohol (CX) (purity 98.8%) in 60% yield. The corresponding *trans,cis*-4,7-diene was obtained in 98% yield on hydrogenation of the triple bond over the Lindlar catalyst in a hexane–THF mixture.[188]

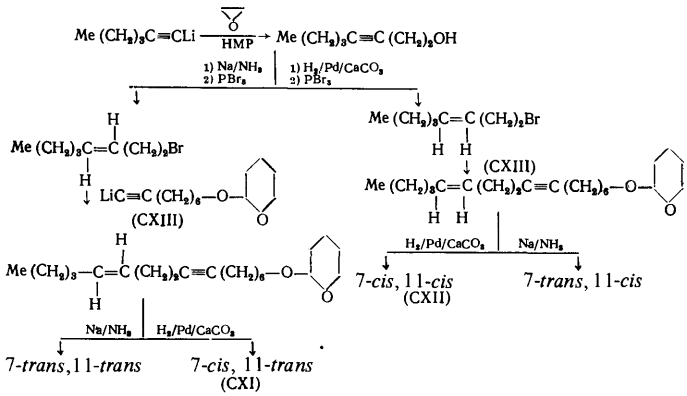
The inactive 4-*trans*,7-*trans*-isomer with an admixture of a mono-olefin (9%) was obtained by reducing the 1,4-enyne (CX) with lithium in liquid ammonia in the presence of ethanol. In the synthesis of *trans,trans*-1,4-dienoic acids it was shown that the reduction with lithium in ammonia without the addition of alcohol leads only to a mixture of *trans*-monoenoic acids.[191] For example, the 6,9-dienoic acid affords under these conditions a mixture of *trans*-6- (15%), *trans*-7- (36%), *trans*-8- (33%), and *trans*-9-monoenoic acids (16%).[191] Consequently such reduction of 1,4-dienes is accompanied by the base-catalysed formation of compounds with conjugated double bonds, which are then reduced to the monoene compounds. When 1,4-enynes were treated with alkali metal amides in ammonia, a rapid rearrangement of the *trans*-isomers to the *cis*-1,3-enynes was noted.[192] Octadeca-9,12-diynoic acid has been successfully reduced to *trans,trans*-octa-9,12-dienoic acid with sodium in a mixture of ammonia and diethyl ether in an autoclave.[185]

The reduction of 1,4-enynes with sodium in an ammonia–THF mixture in the presence of t-butyl alcohol is more stereospecific than in the presence of ethanol.[193] The 1,4-dienes were stabilised by adding 0.1% of 2,6-di-t-butyl-4-methylphenol.

Synthetic *trans,cis,trans*- and *trans,cis,cis*-trideca-4,7,11-trienyl acetates are not active components of the pheromone of *Phthorimaea operculella* but they do give rise to a positive response on the electroantennogram.[1]

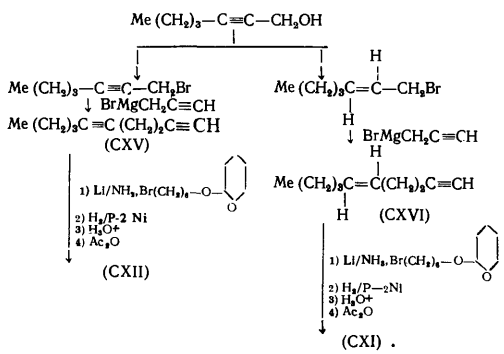
*trans*-10-n-Propyltrideca-5,9-dienyl acetate (propylure) was initially identified as the pheromone of the pink bollworm *Pectinophora gossypiella*, which is a pest on the cotton-plant.[193,194] Synthetic propylure exhibited a very weak biological activity. However, it was later found that the pheromone consists of "gossyplure"—a 1 : 1 mixture of *cis,trans*- and *cis,cis*-hexadeca-7,11-dienyl acetates.[112,193–196] The individual geometrical isomers are inactive.[195]

Synthetic *cis*-hexadec-7-enyl acetate (hexalure) proved to be an attractant of the butterfly *Pectinophora gossypiella*.[197] *cis,trans*-Hexadeca-7,11-dienyl acetate (CXI) has been identified as the pheromone of *Sitotroga cerealella*.[198] The acetate (CXI) and its 7-*cis*,11-*cis*-isomer (CXII) were obtained in a pure form via acetylenic intermediates[197–200] using an acetylenic Grignard reagent[195,201] or with the aid of the Wittig reaction.[200,202] In many studies the mixture was prepared artificially for the purpose of screening, while in others the required 1 : 1 mixture was obtained immediately by the Wittig synthesis.[115] All four possible geometrical isomers were obtained using oct-3-yn-1-ol and the lithium salt of 2-(7-octynyloxy)tetrahydropyran (CXIII):[203]



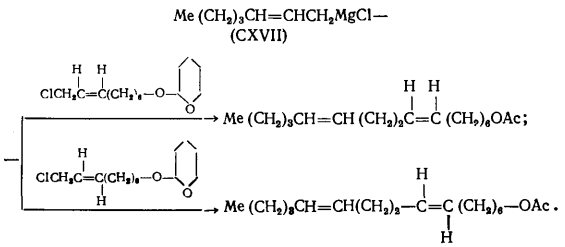
The homoallyl *cis*- and *trans*-oct-3-enyl bromides have been obtained from the corresponding alcohols by treatment with triphenylphosphine dibromide in dioxan (yield 85%) or with $PBr_3$ in a mixture of ether and pyridine (yield 56%). The condensation products were obtained by the reaction of these bromides with the lithio-derivative (CXIII) in dioxan (yield 25%)[198] or in diglyme (yield 66%).[204] The *trans*-configuration of the double bond was achieved by reduction with sodium in ammonia and the *cis*-configuration by hydrogenation over a modified Lindlar catalyst.[198]

The diyne (CXV) (79%) and the enyne (CXVI) (63%) have been obtained respectively by the interaction of propargylmagnesium bromide (CXIV) with 1-bromohept-2-yne and *trans*-1-bromohept-2-ene:[205]

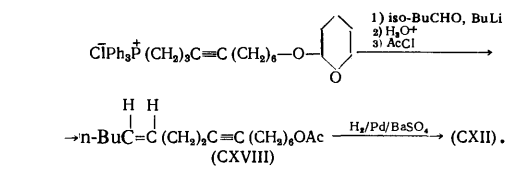


The products of the alkylation of their lithium salts by tetrahydropyranyloxyoctyl bromide were obtained in 62% yield for the diyne (CXV) and 87% for the enyne (CXVI). Acid hydrolysis and partial hydrogenation leads to the pheromone components.[206] Deca-1,5-diyne (CXV) was obtained in 40% yield by the monoalkylation of the monolithium salt of hexa-1,5-diyne with 1-bromobutane in a mixture of HMP and THF.[195] The interaction of the Grignard reagent (CXVII) with *cis*(or *trans*)-allyl chloride in THF leads to a mixture of products with straight and branched chains,[201] the straight-chain product being formed in 20% yield from *cis*-allyl chloride

in the form of a mixture of the 7-*cis*,11-*cis*, and 7-*cis*,11-*trans*-isomers in proportions of 43 : 57:



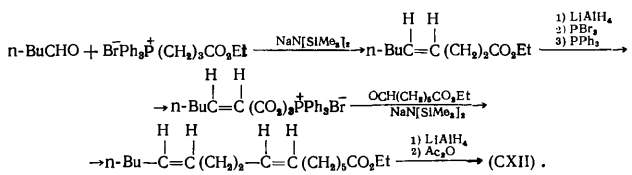
The yield of the branched-chain product diminishes to 50% when the reaction is carried out in a mixture of THF and HMP; the *cis*-11-isomer with a stereochemical purity of 94% is then obtained. Condensation of pentanal with the Wittig reagent derived from 11-tetrahydropyranyloxyundec-4-ynyl chloride leads to the enyne (CXVIII) consisting of 96% of the *cis*-isomer and 4% of the *trans*-isomer: [200]



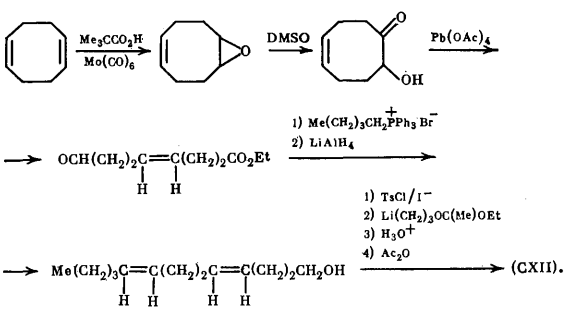
Partial hydrogenation results in the formation of the *cis*,*cis*-isomer (CXII). *trans*,*trans*- and *trans*,*cis*-Hexadeca-7,11-dienyl acetates have been obtained by the isomerisation of bisepoxides on treatment with lithium diphenylphosphide. [207]

The reduction of the 1,5-enyne system with sodium in liquid ammonia, which leads to the *trans*,*trans*- and *trans*,*cis*-7,11-dienes, always affords a mixture of isomers containing 72% of the *trans*,*trans*-dienes, 18% of other dienes, and 5% of cyclic products. [200]

The Wittig reaction where sodium bis(trimethylsilyl)amide in THF is used as the base is highly *cis*-stereospecific (up to 98%): [202]

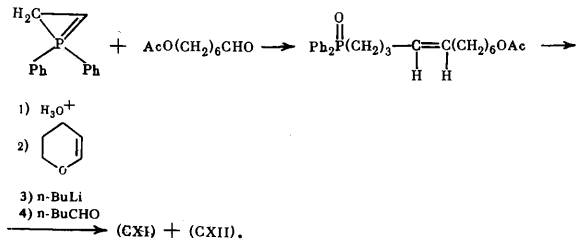


The dependence of the stereospecificity of this reaction on temperature has been observed. Thus at −78 °C the ratio of the *cis*- and *trans*-isomers in the olefinic product is 98 : 2, while at 20 °C it is 94 : 6. The components of gossyplure have been obtained also from *cis*,*cis*-cyclo-octa-1,5-diene. [115] The asymetric rupture of one of the double bonds leads to an intermediate containing not only the necessary functional groups but also a *cis*-double bond:



Next the Wittig reaction with the olefin was carried out and a study was made of the influence of various factors on the stereochemistry of this reaction. [5] It is known that an aliphatic ylide reacts with an aliphatic aldehyde to give mainly *erythro*-intermediates, which are converted into a *cis*-olefin after splitting off triphenylphosphine oxide.

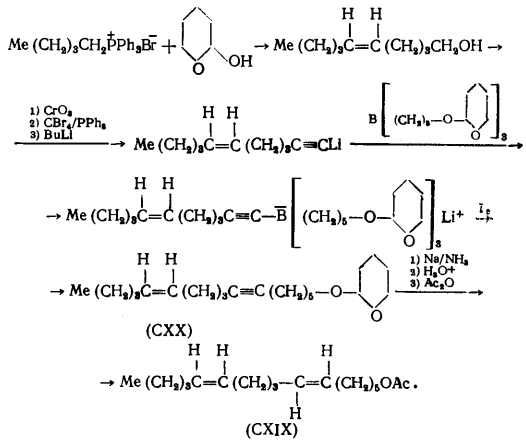
Olefinic phosphine oxides obtained from cyclic phosphonium ylides are of great interest for the synthesis of the components of gossyplure—hexadeca-7,11-dienyl acetates: [209]



When the Wittig reaction was carried out in dipolar aprotic solvents (DMF, DMSO, HMP) both in the presence and absence of a lithium salt, identical results were obtained. In non-polar solvents the stereochemistry of the olefinic products depends on the nature of the inorganic salts. [1,5,209] *trans*,*cis*- and *cis*,*cis*-Octadeca-3,13-dienyl acetates are the pheromones of *Synanthedon pictipes* and *Synanthedon exitiosa*. [210–212] All four isomers of octadeca-3,13-dienyl acetate were obtained via acetylenic intermediates. [213]

*trans*,*cis*-Hexadeca-6,11-dienyl acetate (CXIX) is the pheromone of the oak silkworm *Anthreraea polyphemus* in a 9 : 1 mixture with the corresponding aldehyde. The acetate (CXIX) has been obtained in accordance with an analogous scheme via acetylenic intermediates. [214,215]

Both components of the pheromone of *Antheraea polyphemus* were also synthesised from the enzyme compound (CXX) using the Wittig reaction to generate the *cis*-11-double bond; the *trans*-6-olefin was synthesised by reduction with sodium in liquid ammonia:



The isomeric purity of the resulting *trans*,*cis*-hexadeca-6,11-dienyl acetate and the corresponding aldehyde is in excess of 97%. [216,217]

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# The Role of Molecular Complexes in the Preparation of Highly Pure Materials

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Various aspects of the influence of molecular complexes on the efficiency of two-phase methods for purifying substances have been examined (for the case of the volatile inorganic hydrides of the elements of groups IIIa–VIIa). Data published in the last 10 years on the experimental and theoretical study of intermolecular interactions in these systems have been discussed. Chemical methods for purifying hydrides, including the formation of stable molecular complexes, have been examined briefly. The bibliography contains 172 references.

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## I. INTRODUCTION

Highly pure substances contain individual impurities at the level of $10^{-4}$–$10^{-8}$% and below, and a total concentration of impurities of $10^{-3}$–$10^{-4}$%.[1]

Methods for preparing highly pure materials are based on differences between the properties of the impurity and the substance being purified, which in turn are generally revealed as differences in the interactions between the particles (atoms, molecules, ions) of the impurities and the main material.[2] The forces of interparticle interaction can be classified as long-range (van der Waals) and short-range (chemical or specific).[3] Methods of purification, in turn, can be classified as physicochemical or chemical, according to the type of interactions responsible for the separation effect. Both types of purification method are being intensively developed, and have been the subject of a number of books and reviews (see Refs.2 and 4 and references therein, and also Refs.5–7).

An important case of interactions occupying an intermediate position between van der Waals and chemical interactions is the formation of molecular complexes.[8] This term covers electron donor–acceptor (EDA) complexes or charge-transfer complexes (CTC), and also complexes with hydrogen bonding (H-complexes).

The formation of molecular complexes, taking place against a background of non-specific van der Waals interactions, influences the efficiency of purification processes; previously, however, there was practically no discussion of this question in the literature. The aim of the present review is to examine various aspects of extensive purification processes, associated with the formation of molecular complexes. The examination will be restricted to only a few classes of substance and purification methods. The discussion will deal chiefly with the two-phase methods of fractional distillation and, to a lesser extent, crystallisation, the theory of which in systems with non-specific interactions is most fully developed at the present time.[5,7] Molecular complexes of different stability play an important role in methods of purification by extraction. Since however these methods are relatively unsuitable for preparing highly pure materials, and since there are no rigorous theories to describe two-phase equilibria in extraction systems,[9,10] this group of methods is not examined in the present review.

The materials chosen to examine the influence of the formation of molecular complexes on the efficiency of extensive purification are the volatile inorganic hydrides of the elements of groups IIIa–VIIa. This choice was made for the following reasons. Volatile inorganic hydrides are fairly widely used to obtain highly pure elements and structures based on them.[11,12] In spite of the considerable progress made in their purification,[1,12] however, the removal of some impurities (for example water) still represents a difficult problem. There are indications that in a number of such cases, hydride–impurity molecular complexes may be formed, leading to a decrease in the efficiency of purification. Finally, the weak specific and more particularly non-specific intermolecular interactions (IMI) in systems based on the hydrides examined, although insufficiently studied, have nevertheless been more fully studied at the present time than other classes of substance obtainable in a highly pure state. The review covers data on non-specific and weak specific interactions in volatile inorganic hydrides, obtained by various experimental methods and also by quantum-chemical calculations and semi-empirical estimates.

In spite of these restrictions, the procedure used to analyse the role of molecular complexes is general in character, and can be used to examine other purification methods and other systems.

## II. BASIC IDEAS FROM THE THEORY OF MOLECULAR COMPLEXES

A large number of papers have been devoted to various aspects of the theory and practical utilisation of molecular complexes of both types (EDA and H-complexes). It is sufficient to mention the most important monographs and reviews published chiefly in the last 10 years in the Soviet Union and other countries.[13–20]

The theory of molecular complexes (usually referred to in the literature as the theory of donor–acceptor interaction) was developed by Mulliken in the early fifties and applied to systems consisting of molecules, one of which has a low ionisation potential (the electron donor D) while the other has a high electron affinity (the electron acceptor A). The nature of the interacting orbitals of the donor and acceptor molecules formed the basis for the generally accepted classification of molecular complexes.[20]

Donor–acceptor interactions in the sense of Mulliken's classical theory are closely related to the problem of the hydrogen bond. In H-complexes, the hydrogen atom acts as a bridge joining atoms X and Y, which generally have a high electronegativity: X–H...Y. In the case of organic molecules, the fragment Y may be a π-electron system.

Intermolecular interactions in molecular complexes of both types can be classified as weak ($\Delta E$ = 0.1–1 kcal mole$^{-1}$, $R_{DA(HY)}$ = 0.30–0.35 nm) medium ($\Delta E$ = 5–15 kcal mole$^{-1}$, $R_{DA(HY)}$ = 0.27–0.30 nm), and strong ($\Delta E$ = 20–60 kcal mole$^{-1}$, $R_{DA(HY)}$ = 0.22–0.25 nm).[3,21] Thus the energies of formation of molecular complexes at one extreme are close to those of van der Waals systems ($\Delta E = 10^{-2}$–$10^{-1}$ kcal mole$^{-1}$,

**Table 1.** The impurity composition of volatile inorganic hydrides (mass %).[12]

| Hydride | Impurity | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $B_2H_6$ | $SiH_4$ | $GeH_4$ | $NH_3$ | $PH_3$ | $AsH_3$ | $SbH_3$ | $H_2S$ | $H_2Se$ | HCl |
| $C_2H_4$ | — | $7\cdot10^{-4}$ | $1.1\cdot10^{-1}$ | — | — | $3\cdot10^{-2}$ | $2.6\cdot10^{-2}$ | — | $1.4\cdot10^{-3}$ | — |
| $C_4H_{10}$ | — | $7.5\cdot10^{-4}$ | 0.74 | — | — | — | — | — | — | — |
| $C_2H_5+C_2H_5OH$ | — | $3.5\cdot10^{-2}$ | — | — | — | — | — | — | | — |
| $(CH_3)_2CO$ | — | $1.1\cdot10^{-1}$ | — | — | — | — | — | — | — | — |
| $(C_2H_5)_2O$ | — | $1\cdot10^{-4}$ | — | — | — | — | — | — | — | — |
| $(CH_3)_2O$ | — | $6.8\cdot10^{-5}$ | — | — | — | — | — | — | | — |
| $CH_3OC_2H_5$ | — | $3.5\cdot10^{-5}$ | — | — | — | — | — | — | — | — |
| $C_2H_5Cl$ | — | $5\cdot10^{-4}$ | — | — | — | — | — | — | — | — |
| $CH_3Cl$ | $1.9\cdot10^{-4}$ | — | — | — | — | — | — | — | — | — |
| $CH_3CHO$ | — | $1.4\cdot10^{-4}$ | — | — | — | — | — | — | — | — |
| $CH_4$ | $1\cdot10^{-3}$ | — | 1.2 | — | — | $1.6\cdot10^{-1}$ | — | — | — | $2.6\cdot10^{-3}$ |
| $C_2H_6$ | $2.5\cdot10^{-4}$ | — | 0.51 | — | $2.7\cdot10^{-2}$ | $4.6\cdot10^{-2}$ | — | — | $1.2\cdot10^{-2}$ | — |
| $C_3H_8$ | $2.5\cdot10^{-4}$ | — | 0.33 | $1\cdot10^{-3}$ | — | $4\cdot10^{-4}$ | — | — | $1.2\cdot10^{-2}$ | $7\cdot10^{-4}$ |
| $C_4H_8$ | — | — | $4.2\cdot10^{-2}$ | $5.2\cdot10^{-4}$ | — | $5.2\cdot10^{-2}$ | $3.6\cdot10^{-3}$ | — | $1.4\cdot10^{-2}$ | $9.6\cdot10^{-4}$ |
| $C_6H_6$ | — | — | — | $7\cdot10^{-2}$ | — | — | — | $1.7\cdot10^{-2}$ | — | — |
| $CHCl_3$ | — | — | — | — | — | - | $8.6\cdot10^{-3}$ | — | — | — |
| $C_2H_2$ | — | — | — | — | — | — | $1.2\cdot10^{-3}$ | — | — | $1.2\cdot10^{-1}$ |
| $CS_2$ | — | — | — | — | — | — | — | $1.2\cdot10^{-1}$ | $2.8\cdot10^{-2}$ | — |
| $CO_2$ | — | — | — | — | — | — | — | — | — | $1.1\cdot10^{-2}$ |
| $AsH_3+GeH_4$ | — | $4.5\cdot10^{-3}$ | — | — | — | — | — | — | — | — |
| $B_2H_6$ | — | $4.3\cdot10^{-3}$ | — | — | — | — | — | — | — | — |
| $PH_3+H_2S$ | — | $6.8\cdot10^{-2}$ | — | — | — | — | — | — | — | — |
| HCl | $3.8\cdot10^{-1}$ | $7.3\cdot10^{-3}$ | — | — | $2.5\cdot10^{-2}$ | $3.6\cdot10^{-2}$ | $9\cdot10^{-2}$ | $2\cdot10^{-2}$ | $5\cdot10^{-1}$ | — |
| $NH_3$ | — | $1.5\cdot10^{-3}$ | — | — | — | — | — | — | — | — |
| $SiH_4$ | — | — | $1\cdot10^{-4}$ | — | — | — | — | — | — | — |
| $PH_3$ | — | — | $1\cdot10^{-5}$ | — | — | — | $3.4\cdot10^{-1}$ | — | — | — |
| $H_2O$* | — | — | 1—2 | $5\cdot10^{-1}$ | $7\cdot10^{-1}$ | $8\cdot10^{-1}$ | | 0.5 | 1.1 | $1.8\cdot10^{-4}$ |
| $SiH(OC_2H_5)_3$ | — | — | — | $2.5\cdot10^{-2}$ | — | — | — | — | — | — |

*The concentration of water in unpurified HF reaches 8.4 mass %.

$R$ = 0.30–0.40 nm), and at the other extreme are close to those of chemically combined molecules ($\Delta E$ = 80–100 kcal mole$^{-1}$, $R$ = 0.10 nm).

Table 1 gives a number of typical impurities in unpurified volatile inorganic hydrides of elements of groups IIIa–VIIa.[12] In spite of the fact that the impurity composition of the hydrides depends to a large extent on the method of synthesis, it is possible to distinguish two groups of impurity in these compounds: inorganic impurities, including the hydrides of analogue elements, higher hydrides, and various gases (CO, $N_2$), and organic impurities, including saturated, unsaturated, and aromatic hydrocarbons, and also hydrocarbons containing heteroatoms with a lone pair of electrons. All this is responsible for the complex character of the IMI in the hydrides being considered. For highly pure hydrides containing most impurities at the level of $10^{-5}$–$10^{-7}$ mass %, it is mainly the weak specific interactions of the hydride–hydride and hydride–impurity type that are important. In starting materials containing from 0.5–1.0 mass % to $10^{-5}$ mass % impurities (Table 1), impurity–impurity molecular complexes are probably also formed.

As noted above (section I), the weak specific interactions leading to the formation of molecular complexes are present against a background of non-specific van der Waals interactions. It is therefore appropriate to discuss in more detail the contributions made to the energy of the interaction of a pair of molecules of a volatile inorganic hydride by specific and non-specific interactions.

The van der Waals interactions in volatile inorganic hydrides are usually characterised quantitatively using the familiar Lennard-Jones potential. Since the model is approximate, the numerical values of the parameters of the potential $\varepsilon$ and $\sigma$ depend on the set of properties from which they are determined.[3] Since the purification processes examined below are based on phase equilibria, it is appropriate to use the values of $\varepsilon$ and $\sigma$ calculated from the vapour pressure and the density of the liquid on the liquid–vapour equilibrium line.[5] The relationships required for this were obtained in Ref.22; Table 2 gives the values of $\varepsilon$ and $\sigma$ obtained in the work cited for volatile inorganic hydrides. The values of $\varepsilon$ for different substances lie mainly in the range 400–800 kcal mole$^{-1}$, and the values of $\sigma$ in the range 0.30–0.45 nm. The values given are the effective values, including the contribution from weak specific interactions when these are present. Specific interactions have comparatively little influence on the magnitude of $\sigma$, but have a considerable influence on the value of the parameter $\varepsilon$, characterising the depth of the potential well.

**Table 2.** The parameters of the Lennard-Jones potential for the volatile inorganic hydrides of the elements of groups IIIa–VIIa.[22]

| Substance | $\epsilon$, cal mole$^{-1}$/$\sigma$, nm | Substance | $\epsilon$, cal mole$^{-1}$/$\sigma$, nm |
|---|---|---|---|
| $CH_4$ | 296/0.374 | $NH_3$ | 723/0.330 |
| $SiH_4$ | 443/0.398 | $PH_3$ | 517/0.399 |
| $GeH_4$ | 503/0.426 | $AsH_3$ | 584/0.407 |
| $SnH_4$ | 604/0.444 | $SbH_3$ | 719/0.427 |
| $H_2O$ | 882/0.305 | HF | 918/0.312 |
| $H_2S$ | 614/0.372 | HCl | 471/0.352 |
| $H_2Se$ | 666/0.388 | HBr | 588/0.375 |
| $H_2Te$ | 767/0.426 | HI | 674/0.401 |

General information on the structure and the nature of the chemical bonding in the molecules of the hydrides of the elements of groups IIIa–VIIa [11] can be used in a preliminary discussion of their tendency to form molecular complexes. The chief characteristic of the hydrides is the presence of a hydrogen atom forming a covalent bond with the central atom of the element. In the examination of these compounds, therefore, it is necessary first of all to take account of the tendency for an intermolecular hydrogen bond to be formed. In addition, the hydrides of boron and aluminium may act as strong $\nu$-type electron acceptors in EDA complexes, using the unoccupied $p$ orbitals of the B and Al atoms.

The polarity of the bonds in the hydrides increases on going from left to right along the periods. The ability of these compounds to form intermolecular H-bonds should increase in the same order. On the other hand, the polarity of the bond decreases on going down the groups, and this should lead to a decrease in the proton-donor power of the hydrides of periods 3–7. The elements of groups Va and VIa have lone pairs of electrons, so that the corresponding hydrides, having low ionisation potentials,[23] can not only form intermolecular H-bonds but also act as $n$-type electron donors towards inorganic and organic electron acceptors.

This is illustrated by the values of $\varepsilon$ given in Table 2. The systematic decrease down the groups in the values of $\varepsilon$ for the hydrides of the elements of groups Va–VIIa, due to the decrease in the contribution of van der Waals interactions, breaks down for ammonia, water, and hydrogen fluoride, because of the large contribution made to the value of $\varepsilon$ by the energy of the hydrogen bond, which is much greater than the corresponding values for phosphine, hydrogen sulphide, and hydrogen chloride. No significant change in the contribution of H-bonds is observed on going from left to right along periods 3–5.

Experimental and theoretical data on the ability of the volatile inorganic hydrides of the elements of groups IIIa to VIIa to form molecular complexes are examined in more detail below. Particular attention will be paid to the systems in Table 1, or related systems.

## III. TWO-PHASE METHODS OF EXTENSIVE PURIFICATION AND THE FORMATION OF MOLECULAR COMPLEXES

Among the physicochemical methods of extensive purification used at present, two-phase distillation and crystallisation methods have found extensive application. The difference between the compositions of the equilibrium phases is characterised by the distribution coefficient of the impurity:

$$K^{vl} = x_2^v/x_2^l;\ K^{sl} = x_2^s/x_2^l \qquad (1)$$

where $x_2$ is the concentration of the impurity in the vapour (v), liquid (l), or solid (s) phases (in mole fractions). The phase equilibrium condition gives the relationship between the distribution coefficients and the chemical potentials of the impurities in the equilibrium phases. Thus the study of the influence of specific interactions on the efficiency of two-phase purification methods is directly related to the study of their influence on the thermodynamic properties of dilute solutions. The methods used for this purpose have been reviewed,[24] and their details will not be discussed further. Interesting data have been published[25] on the purification of the chlorides of various elements tending to form complexes.

Before analysing the influence of specific interactions, the nature of two-phase equilibria in dilute solutions with non-specific interactions can be discussed briefly. A statistical-thermodynamic description of phase equilibria in dilute solutions with non-specific interaction between the molecules, and methods for calculating the distribution coefficient based on it, have been described.[5–7,24] From these methods, that based on the theory of conformal solutions can be selected,

since it is simple and at the same time sufficiently exact.[26,27] By applying this method to a solution for which the interaction between the molecules is described by the Lennard-Jones potential, an expression for the liquid–vapour distribution coefficient has been found in the approximation of an ideal vapour phase.[27,28] Here, only the quantities on which the distribution coefficient depends will be given:

$$K^{vl} = f\left(\frac{kT}{\varepsilon_{11}}, \frac{\varepsilon_{21}}{\varepsilon_{11}}, \frac{\sigma_{21}}{\sigma_{11}}\right) \quad (2)$$

where $T$ is the temperature.

The parameters of the interaction potential of the particles of the impurity and the base are given by the equations:

$$\sigma_{21} = (\sigma_{11}+\sigma_{22})/2;\ \varepsilon_{21} = \xi(\varepsilon_{11}\varepsilon_{22})^{1/2} \quad (3)$$

where $\varepsilon_{ii}$ and $\sigma_{ii}$ are the parameters characterising the interaction of the particles of the base ($i = 1$) and the impurity ($i = 2$) components. The parameter $\xi$ in the Lorentz–Berthelot combination rules (3) for solutions with non-specific interactions is usually taken as 1.

Table 3 compares experimental data with the results of calculations of the distribution coefficients from Eqn.(2) for a number of systems in which specific interactions are weak or non-existent. The calculation of the distribution coefficient using the Lennard-Jones potential for $\xi = 1$ in most cases gives correctly the nature of the deviations from Raoult's law, so that this potential can be regarded as a satisfactory effective potential for this case. The deviations from 1 in the values of $\xi$ found from the values of $K^{vl}_{expt}$ are relatively small, confirming that there are no appreciable donor–acceptor interactions between the components of the solutions studied. The values of $\xi \leqslant 0.97$ are apparently due to the inaccuracy of the values of the experimental distribution coefficient used.

**Table 3.** Results of the calculation of the distribution coefficient in systems based on volatile inorganic hydrides at their normal boiling points.[6]

| System | $K^{vl}_{id} = p_{02}/p_{01}$ | $K^{vl}$ | $K^{vl}_{expt}$ | $\xi$ |
|---|---|---|---|---|
| $SiH_4$—$GeH_4$ | 0.23 | 0.26 | 0.26 | 1.00 |
| $SiH_4$—$PH_3$ | 0.22 | 0.26 | 0.23 | **1.01** |
| $SiH_4$—$AsH_3$ | 0.05 | 0.075 | 0.078 | **1.00** |
| $SiH_4$—$H_2S$ | 0.02 | 0.076 | 0.093 | 0.99 |
| $SiH_4$—$B_2H_6$ | 0.28 | 0.26 | 0.73 | 0.95 |
| $SiH_4$—HCl | 0.17 | 0.35 | 0.35 | 1.00 |
| $SiH_4$—$C_2H_4$ | 0.60 | 0.63 | 0.76 | 0.99 |
| $SiH_4$—$C_2H_6$ | 0.23 | 0.46 | 0.26 | 1.03 |
| $SiH_4$—$C_3H_8$ | 0.009 | 0.013 | 0.03 | 0.97 |
| $GeH_4$—$SiH_4$ | 2.92 | 3.11 | 2.52 | 1.01 |
| $GeH_4$—$AsH_3$ | 0.27 | 0.33 | 0.38 | 0.99 |
| $GeH_4$—$H_2S$ | 0.18 | 0.32 | 0.31 | 1.00 |
| $GeH_4$—$C_2H_4$ | 2.26 | 2.09 | 2.23 | 1.00 |
| $GeH_4$—$C_2H_6$ | 1.01 | 1.62 | 1.21 | 1.02 |
| $GeH_4$—$C_3H_8$ | 0.071 | 0.082 | 0.081 | 1.00 |
| $PH_3$—$AsH_3$ | 0.29 | 0.30 | 0.68 | 0.96 |
| $AsH_3$—$PH_3$ | 2.57 | 2.83 | 3.03 | 1.00 |

Notes. $p_{01}$ and $p_{02}$ are the saturated vapour pressures of the pure base and the impurity; the values of the parameter $\xi$ in Eqn.(3) were found from Eqn.(2) using the experimental values of the distribution coefficient $K^{vl}_{expt}$.

Donor–acceptor interactions make the phase equilibria more complex. In solutions whose components form molecular complexes, azeotropes are fairly frequently produced. In this case, the estimation of the distribution coefficient from Raoult's law may lead to a qualitatively incorrect result, namely to an incorrect indication of the phase in which the impurity is concentrated.

The influence of specific interactions on the distribution coefficients can be analysed in two ways. In the first, the interaction potential, which in some form takes account of the specific components, is directly related to the distribution coefficient. In the second, explicit account is taken of the presence of various complexes and associates formed as a result of specific interactions, and the expression for the distribution coefficient includes the equilibrium constant of the complex formation process.

In the first approach, the main consequences of the existence of specific interactions follow directly from Eqns. (2) and (3) when the depth of the potential well $\varepsilon_{ij}$ is separated into non-specific $\varepsilon^0_{ij}$ and specific $\delta\varepsilon_{ij}$ components:

$$\varepsilon_{ij} = \varepsilon^0_{ij} + \delta\varepsilon_{ij};\quad \varepsilon^0_{ij} = (\varepsilon^0_{ii}\varepsilon^0_{jj})^{1/2} \quad (4)$$

(for the separation of these components, see also section VI). It follows from Eqns.(4) and (5) that

$$\xi = \frac{\varepsilon^0_{21} + \delta\varepsilon_{21}}{[\varepsilon^0_{11}\varepsilon^0_{22} + (\varepsilon^0_{11}\delta\varepsilon_{22} + \varepsilon^0_{22}\delta\varepsilon_{11} + \delta\varepsilon_{11}\delta\varepsilon_{22})]^{1/2}}. \quad (5)$$

For $\delta\varepsilon_{ij} = 0$, $\xi = 1$. A relatively small contribution of specific interactions to $\varepsilon_{21}$ gives values of $\xi < 1$, and increase in the contribution $\delta\varepsilon_{21}$ (or decrease in $\delta\varepsilon_{ii}$) gives $\xi > 1$. It follows from Eqn.(3) that decrease in $\xi$ leads to an increase in the value of $K^{vl}$, and a positive azeotrope may be produced, whereas increase in $\xi$ decreases $K^{vl}$ and leads to the production of a negative azeotrope.

Special mention may be made of cases when specific interactions lead to qualitative (from the viewpoint of the sign of $\ln K^{vl}$) deviations from Raoult's law. If the boiling point of the impurity component is higher than that of the main component, these qualitative deviations ($K^{vl}_{id} < 1$, $K^{vl}_{expt} > 1$) are produced when $\xi < 1$ (for example if $\delta\varepsilon_{11} = \delta\varepsilon_{21} = 0$ and $\delta\varepsilon_{22} \neq 0$). If the boiling point of the impurity component is lower than that of the main component, qualitative deviations ($K^{vl}_{id} > 1$, $K^{vl}_{expt} < 1$) are observed when $\xi > 1$ (for example if $\delta\varepsilon_{11} = \delta\varepsilon_{22} = 0$ and $\delta\varepsilon_{21} \neq 0$).

The quantitative estimation of the distribution coefficients of impurities in solutions in which the interactions have a specific component $\delta\varepsilon_{11}$ can be carried out using the methods[5–7] for solutions with non-specific interactions only when the specific component makes a small contribution: $\delta\varepsilon_{11} \lesssim 0.1\varepsilon_{11}$. In other cases, quantitative estimates require more rigorous models of the impurity–base and base–base interaction potentials (see section VI).

The properties of dilute solutions with specific interactions can be examined further by taking explicit account, via the equilibrium constants, of the processes of molecular complex formation. When the energy of formation of impurity–impurity and impurity–base complexes is sufficiently high, when their lifetime becomes greater than the characteristic time of the thermal motions in the liquid, $\tau \cong 10^{-12}$ s, it is reasonable to regard the complexes as different molecular forms of the impurity.

The formation of a molecular complex can be represented by the equation

$$iA + jB \rightleftharpoons A_iB_j \quad (6)$$

where A is the main component, and B the impurity. The equilibrium constants of the complex formation reactions in the vapour $K_V$ and liquid $K_l$ phases

$$K_{v,l} = \frac{[A_iB_j]_{v,l}}{[A]^i_{v,l}[B]^j_{v,l}} \quad (7)$$

and the distribution coefficients of the impurity in the monomeric and associated forms

$$K_m^{vl} = [B]_v/[B]_l;\ K_{ass}^{vl} = [A_iB_j]_v/[A_iB_j]_l \qquad (8)$$

can be introduced. The generalised distribution coefficient of the impurity[29,30] [compare Eqn.(2)]:

$$K^{vl} = \frac{[B]_v + j[A_iB_j]_v}{[B]_l + j[A_iB_j]_l} \qquad (9)$$

characterises the equilibrium distribution of the impurity B, irrespective of its specific molecular form.

Eqn.(9) can be examined for two particular cases: the formation of impurity–base and impurity–impurity dimers. In the first case, Eqn.(9) gives two equivalent relationships:

$$K^{vl} = \frac{1 + K_v}{1 + K_l} K_m^{vl};\ K^{vl} = \frac{(1 + K_v)K_l}{(1 + K_l)K_v} K_{ass}^{vl} \qquad (10)$$

It follows from Eqns.(10) that $K^{vl}$ takes values intermediate between $K_m^{vl}$ and $K_{ass}^{vl}$. When $K_v$ and $K_l \ll 1$, $K^{vl} \cong K_m^{vl}$, and when $K_v$ and $K_l \gg 1$, $K^{vl} = K_{ass}^{vl}$. Similarly, the cases where $K_V \gg K_l$ and $K_V \ll K_l$ reduce only to a renormalisation of the quantity $K^{vl}$.

Eqn.(9) has more interesting consequences when impurity–impurity dimers are formed:

$$K^{vl} = K_m^{vl} \frac{1 + 2K_vK_m^{vl}[B]_l}{1 + 2K_l[B]_l} \qquad (11)$$

In this case, $K^{vl}$ depends on the concentration. In the absence of specific interactions, the distribution coefficient becomes independent of concentration at $[B]_l \leqslant 10^{-2}$.[24] It follows from Eqn.(11) that at high values of the equilibrium constants of the complex formation process, a concentration dependence may also be observed at lower concentrations. It also follows from Eqn.(11) that $K^{vl} = K_m^{vl}$ as $[B]_l \to 0$ as the equilibrium for the dimerisation is displaced towards the formation of the monomers with decrease in the concentration of the impurity. Since usually $K_v \leqslant 1$ and $K_m^{vl} \cong 1$, Eqn.(11) shows that for a concentration dependence in the range $[B]_l \cong 10^{-3}$, it is necessary that $K_l \cong 5 \times 10^2$.

Quantitative estimates of the proportions of impurities in different molecular forms require methods for calculating the equilibrium constants in the liquid phase. These calculations can be based on published rigorous statistical-thermodynamic expressions[31] for the quantities $K_l$ (see also the published review[32]).

The possibility of considerable deviations from the laws of ideal solutions and the production of different molecular forms of the impurities have a significant influence on the behaviour of impurities during purification, so that their study is important for the practical preparation of highly pure materials. It also follows that the chief question which must be investigated is whether molecular complexes are formed in the given system, and if so, whether they are stable or unstable.

Since at present there is no single theory which might be used to predict reliably the formation of donor–acceptor complexes (including H-complexes) the question raised can be answered by undertaking: 1) an experimental study of complex formation under the actual conditions of the given method of purification, or, if this is difficult, under model conditions with subsequent extrapolation of the results obtained to the real conditions; and 2) a theoretical (quantum-chemical) calculation, in a given approximation, of the energy of formation of the complex (the energies of the interaction of the complex-forming molecules) and other thermodynamic parameters.

## IV. EXPERIMENTAL METHODS FOR STUDYING MOLECULAR COMPLEXES

Practically all present-day physicochemical methods are used in the study of molecular complexes. Exhaustive reviews of these topics have been published.[13–16,18,20] The information on weak EDA and H-complexes is of greatest interest. At the present time, therefore, most experimental studies of molecular complexes are aimed at increasing the sensitivity of existing methods both by introducing new techniques and by improving existing methods. Molecular complexes are studied in all states of aggregation. Since their formation is exothermic, and since the reactions take place with a decrease in the number of moles, the most significant results should be obtained by using low temperatures and/or high pressure.

All methods of studying molecular complexes can be provisionally divided into two large groups: spectroscopic (in practically all ranges of the electromagnetic spectrum) and non-spectroscopic (calorimetry, chromatography, measurement of dipole moments, second virial coefficients, etc.).

The first group of methods can be examined in slightly more detail. The traditional method of studying EDA complexes of different stability is electronic spectroscopy in the ultraviolet or visible ranges, used to record the charge-transfer (CT) band. The spectroscopic characteristics of the CT bands are used to determine the thermodynamic characteristics of EDA complexes, usually in the liquid or gas phases (extensive reviews of these data have been published,[14,15,23,68] chiefly for organic compounds). This method has been used to study various complexes of hydrogen sulphide.[34] It can obviously also be used for other systems based on hydrides having a lone pair of electrons ($n$-donors).

The use of vibrational spectroscopy to study EDA complexes is most effective when strong donor–acceptor bonds are formed, since it is only then that the corresponding intermolecular vibrations are completely characteristic. Far infrared spectroscopy is particularly promising in this connection.[35] On the other hand, infrared spectroscopy is still the chief source of information on the hydrogen bond in H-complexes of different stability, as indicated by recent reviews.[18,20,36] Measurement of the spectroscopic characteristics of the $\nu_{XH}$ stretching band (its displacement to shorter wavenumbers and the increase in its strength when a complex is formed) gives valuable information on the nature of the hydrogen bond and the thermodynamic characteristics of H-complexes in the liquid or gas phase.

Comparatively few experimental papers have been published on the study of H-complexes formed by the volatile inorganic hydrides of the elements of groups IIIa–VIIa in solution or in the gas phase (see Table 5). Exceptions are water (although in this case most attention has been paid to associates $(H_2O)_n$ [37–39]) and, to some extent ammonia and hydrogen halides.[40,41] The spectroscopic study of intermolecular interactions in these systems encounters considerable difficulty. Thus most complexes based on the hydrides being considered are very weak (see section V). At the same time, in systems such as $H_2O$–HCl, $NH_3$–HCl, and $NH_3$–$H_2O$ at high concentrations of the components in solution in a polar substance or even in the gas phase, protonated species (ion pairs) may be formed.[42] The nature of the IMI in these systems should be different, however, in dilute solutions based on one of these components.

Extensive possibilities for studying H-complexes of both types (with and without proton transfer) are provided by infrared spectroscopy in low-temperature matrices of nitrogen and noble gases. This method is now being used in many laboratories (see the published reviews[43,44]). Unfortunately, the H-complexes of volatile inorganic hydrides have been insufficiently studied by this method. Data on the $\nu_{HHal}$ stretching wavenumbers and the relative wavenumber displacements $\Delta\nu/\nu$ in the spectra of H-complexes of hydrogen halides with the molecules of a number of substances which are potential impurities in these compounds have been reviewed[45] (see Table 1). Attempts have been made to establish correlations between the properties of H-complexes and the molecular characteristics reflecting the nature of the electronic structure of the partner molecules.[41,45,46] Most frequently, use is made of the proton-acceptor (electron-donor) power of the base PA, determined by various methods. Although the absolute magnitude of the relative wavenumber displacement of the $\nu_{HHal}$ band of the complex generally increases with increase in the PA, there is no simple relationship between these quantities. The H-bonds formed by hydrogen halides with molecules containing atoms with lone pairs of electrons (water, dimethyl ether, etc.) are fairly strong.

The study of IMI in systems based on water by infrared spectroscopy in low-temperature matrices is important, since, as can be seen from the data in Table 1, water is a universal impurity, most difficult to remove, in all volatile inorganic hydrides, and also in many other volatile compounds (for example the chlorides of the elements of groups IIIa–Va [47]). The study of these complexes by ordinary infrared spectroscopic methods is fairly complicated. On the other hand, comparatively few papers on matrix-isolation studies have been published. Most have been devoted to the dimers $(H_2O)_2$ and the polymers $(H_2O)_n$ (see the published review[48] and other papers[49,53]).

Table 4 gives the wavenumbers of the stretches ($\nu_1$ and $\nu_3$) and deformations ($\nu_2$) of the O–H bond in a molecule of free water and water combined with proton acceptors (argon matrix). Like the H–Hal stretching wavenumbers, $\nu_1$ and $\nu_3$ decreases relative to monomeric water on complex formation, and the magnitude of the wavenumber shift $\Delta\nu$ characterises in a definite sense the stability of the H-complexes formed. According to this characteristic, the strength of the H-bonds in matrix-isolated water systems changes in the order:

$$NH_3 < (CH_3)_2O > H_2O > HCl \approx H_2S \approx Cl_2 > CO_2$$

**Table 4.** Wavenumbers of the principal vibrations of the $H_2O$ molecule ($cm^{-1}$) in the free state and combined in a complex[50–52,54–56] (the type of matrix is given in brackets).

| Type of vibration | $H_2O$ (monomer) | | | | Complex $H_2O$–X | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | (Ar) | ($N_2$) | X=$(CH_3)_2O$ (Ar) | X=HCl (Ar) | X=$H_2S$ ($N_2$) | X=$H_2O$ (Ar) | X=$CO_2$ ($N_2$) | X=$Cl_2$ ($N_2$) | X=$NH_3$ ($N_2$) |
| $\nu_1$ | 3638 | 3634 | 3506 | 3631 | 3628 | 3575 | 3632 | 3631 | 3414–3374 |
| $\Delta\nu_1$ | — | — | 132 | 7 | 6 | 63 | 2 | 7 | 240 (ср.) |
| $\nu_2$ | 1589 | 1597 | 1615 | 1590 | 1597 | 1611 | 1598 | 1597 | — |
| $\nu_3$ | 3734 | 3728 | 3706 | — | 3719 | 3710 | 3725 | 3726 | 3697 |
| $\Delta\nu_3$ | — | — | 28 | — | 9 | 24 | 2 | 8 | 31 |

Among the systems of interest for the present review, mention may be made of published data on the complexes formed by hydrogen sulphide and ammonia, obtained by matrix-isolation methods.[53,54,56–60]

The chief disadvantage of the matrix-isolation method is that in the rigid matrix the systems being studied are in a non-equilibrium state, so that the experimental determination of the thermodynamic functions of the complex is impossible. An alternative method of study is provided by infrared cryospectroscopy, where liquid noble gases, which are highly transparent, are used as solvents.[61–64] In the study of the state of impurities in inorganic hydrides and similar compounds which have a simple molecular structure and which are liquefied at low temperatures, it is probably possible to use the compounds themselves as solvents, at temperatures close to the boiling point (if they are transparent in the given spectral range).

Important information on the structural, electric, and in some cases energy characteristics of the weak molecular complexes of simple molecules in the gas phase at low pressure can be obtained by various forms of rotational spectroscopy developed in the last ten years: microwave spectroscopy with Stark modulation; electron-resonance spectroscopy in molecular beams; and pulse microwave Fourier spectroscopy in a supersonic gas beam with adiabatic expansion from a vessel at high pressure.[65–67] These methods have been used to study a number of systems containing the hydrides of the elements of groups Va–VIIa and the molecules of potential impurities (see for example Refs.65 and 68).

In non-spectroscopic methods for studying molecular complexes, in contrast to spectroscopic methods, the thermodynamic parameters of the complexes are determined by measuring properties of the solution which depend only on the number of particles in it, and not on the physical parameters of the particles of different type. An important representative of this group of methods is gas–liquid chromatography.[69,70] The advantages of this method are the direct determination of the equilibrium constants from the retention volumes without the more complicated measurement of the concentrations of the substances in two phases, and also the possibility of working with low concentrations at which the laws of dilute solutions are applicable. This last feature is particularly important in the study of the state of impurities in highly pure volatile substances, and gas chromatography has for long been used successfully for the quantitative analysis of these materials.[71]

The above brief review of various physical methods for studying molecular complexes shows that it is still necessary and important to identify and determine the thermodynamic properties of both EDA and H-complexes and complexes formed in a large excess of one of the components (in dilute solution) or at equivalent ratios of the components at low temperatures ($NH_3$–HCl, $NH_3$–$H_2O$, etc.).

At the same time, primary information on the energy and structure of these complexes can also be obtained from quantum-chemical calculations. The number of published papers in this field, including those devoted to the complexes formed by the volatile hydrides of the elements of groups IIIa–VIIa, is increasing continuously. Some of these will be examined in the next section.

## V. QUANTUM-CHEMICAL METHODS FOR STUDYING MOLECULAR COMPLEXES

The use of modern methods of quantum chemistry to solve the problems being discussed in the present review, related to the theory and practice of the preparation of highly pure materials, is necessary for the following reasons. Firstly, after establishing the impurity composition of the substance being purified, it is necessary to estimate quantitatively the

possibility of specific interaction beween the impurity molecules and the molecules of the main material, and of impurity–impurity interactions when the concentration of individual impurities is appreciable. Calculation methods now available often make it possible to obtain information on at least the relative stability of possible associates more easily than by experiment. It must be remembered, however, that the result obtained will relate to an isolated molecule of the complex, without allowance for the solvation energy.

Secondly, one of the principal problems in the theory of the preparation of highly pure materials is the development of reliable methods of calculating the distribution coefficient of an impurity for two-phase purification methods. In most cases, increase in the accuracy of calculations of the distribution coefficient requires primarily refinement of the interaction potentials. Quantum chemistry can now be used to calculate these potentials. Quantum-chemical interaction potentials can be used for the *a priori* estimation of other quantities characterising the preparation of a highly pure substance: solubility, diffusion coefficient, rate of the introduction of impurities from the material of the apparatus into the substance being purified.

The most reliable data on the energy and geometry of molecular complexes (EDA and H-bonded) are obtained from non-empirical (*ab initio*) calculations by the method of molecular orbitals (MO) in the self-consistent field (SCF) approximation. The present state of different versions of these calculations has been reviewed.[15,20,72–74] The present section deals briefly with the principal concepts of the method and discusses published data on the stability of some of the two-component systems with weak specific interactions discussed in Table 1. Since they are particularly important for the problems being discussed in the present review, topics related to the construction of quantum-chemical IMI potentials are discussed separately in the next section.

In the MO SCF approximation, a molecular complex is regarded as a supermolecule whose energy of formation (the IMI energy) is equal to the difference between the total energy of the complex $E_{DA}$ and the energies of the components $E_D$ and $E_A$:

$$\Delta E = E_{DA} - E_D - E_A$$

The accuracy of non-empirical calculations of $\Delta E$ depends chiefly on the number of basis atomic orbitals (AO) used to construct the MO. The generally accepted notation used below for different basis sets is explained, for example, in Ref.74. In the SCF approximation, no account is taken of the correlation of the motion of the electrons at each moment of time, as a result of which the electrons in individual orbitals are situated as far as possible from one another. The correlation energy $\Delta E^{corr}$ corresponding to this process constitutes only a small fraction of the total energy $\Delta E$, but allowance for it is important in rigorous calculations of the stability of complexes. For example, for the dimer $(H_2O)_2$, $\Delta E = -4.5$ kcal mole$^{-1}$, and the contribution of the correlation energy is $-1.1$ kcal mole$^{-1}$.[75] In practice, allowance for $\Delta E^{corr}$ reduces to the calculation of the dispersion energy using either perturbation theory[76] or multipole expansion, in which the coefficients are determined from experimental data on the polarisability of the molecules.[77] An alternative method of taking account of the correlation energy is the configuration interaction (CI) method.[75,78] Even when a minimum basis set is used without allowance for correlation energy, non-empirical calculations are usually carried out for molecules containing a comparatively small number of atoms (10–15) belonging to the second and third periods.

For more complex molecules and complex compounds, extensive use is made of semi-empirical methods, usually based on the neglect of differential orbital overlap and using SCF equations (CNDO, INDO, etc. methods).[79] These methods are much less laborious and therefore more accessible. For molecular complexes, however, these methods give absolute values of the energy of IMI which are systematically several times too high. Data on the use of these methods to calculate the energy and geometry of EDA and H-complexes have been reviewed.[74,80] Recently, interesting parametrisation schemes for familiar versions of the CNDO and INDO methods have been proposed, making it possible to obtain various geometric and energy characteristics of complexes containing hydrogen bonds of the type O–H...O, O–H...N, and N–H...O.[81,82] Semi-empirical methods are useful for estimating the relative characteristics of IMI in a series of structurally related molecular complexes. Thus it is possible to obtain information fairly rapidly on the relative stability of practically all the hydride–impurity and impurity–impurity dimers given in Table 1.

The results of non-empirical calculations of the complex-forming power of the molecules of the hydrides of the elements of the second and third periods, given in Table 1, both with respect to one another (dimers) and with respect to various inorganic and organic molecules (heterodimers) can be discussed in more detail. Detailed calculations have been carried out for complexes involving $BH_3$, $AlH_3$, $NH_3$, $PH_3$, $H_2O$, $H_2S$, HF, and HCl. There are no published data on the quantum-chemical description of the IMI in silane, although a number of papers (for example Refs.83 and 84) give detailed calculations of the structure and properties of the $SiH_4$ molecule by non-empirical methods.

**Table 5.** Energies of the hydrogen bonds (kcal mole$^{-1}$) for the hydrides of the elements of the second and third periods, from the results of non-empirical quantum-chemical calculations*.[85–87]

| Electron donor | Proton donor | | | | | |
|---|---|---|---|---|---|---|
| | $NH_3$ | $PH_3$ | $H_2O$ | $H_2S$ | HF | HCl |
| $NH_3$ | 4.3 (4.5±0.4) [88] | 1.2 | 8.9 | 4.4 | 16.3 | 10.8 (15.2±±0.3) [89] |
| $PH_3$ | 2.2 | 0.8 | 4.0 | 2.1 | 6.9 | 4.3 |
| $H_2O$ | 4.1 | 1.1 | 8.1 (5,1) [91]; (6±3) [90] | 3.8 | 13.4 | 8.2 |
| $H_2S$ | 2.1 | 0.6 | 3.9 | 1.8 (1.7±0.3) [92] | 5.8 | 3.5 |
| HF | 3.6 | 1.0 | 5.4 | 2.5 | 5.8 (5–7) [93] | 4.6 |
| HCl | 1.6 | 0.4 | 2.5 | 1.1 | 3.4 | 2.0 |
| $H_2CO$ | 1.4 | 0.2 | 3.4 | 0.6 | 6.2 | 5.3 |

*The experimental values of the energies of the complexes (from infrared spectroscopy) are given in brackets.
Note. Numbers in square brackets denote references (Ed. of Translation).

As already noted, the chief aim of this section of the present review is a comparative analysis of the stability of weak complexes of various hydrides, that is a comparison of the energies of IMI found under identical conditions. The data obtained for ~40 dimers and heterodimers in a 4-31G restricted basis set[85–87] are of particular interest in this connection (Table 5). The results of these calculations agree satisfactorily with experimental data (gas-phase infrared spectra). According to published estimates,[86] the data given in Table 5 are all slightly high (5–50%), relative to

the experimental data and the best non-empirical results, and the more stable the complex, the greater the error. Nevertheless, these data lead to the following conclusions.

1. All the hydrides considered tend to undergo self-association by H-bonds of low or medium energy.

2. The tendency to form dimers decreases in the order $H_2O > HF > NH_3 > HCl > H_2S > PH_3$. The energy of the hydrogen bond varies from $-16.3$ kcal mole$^{-1}$ for $HF-NH_3$ to $-0.4$ kcal mole$^{-1}$ for $PH_3-HCl$. The strongest bonds are formed with hydrogen fluoride or hydrogen chloride as proton donor.

3. The proton-acceptor power decreases sharply on going from the hydrides of the second period to those of the third period.

4. In the heterodimers of the hydrides of the elements of the second period, ammonia shows electron-donor properties with respect to water and hydrogen fluoride; water acts as electron donor only towards HF. In the heterodimers of the hydrides of the third period, the hydride of an element of a group with a smaller number acts as an electron donor with respect to that of an element of a subsequent group. For the heterodimers of the hydrides of the elements of the second and third periods, the following apply: HCl is a proton donor towards $NH_3$, $H_2O$, and HF; $H_2S$ is a proton donor towards $NH_3$, but an electron donor in the complex with HF. In its reaction with $H_2O$, hydrogen sulphide shows both electron-donor and proton-donor properties, to equal extents. Finally, $PH_3$ forms weak complexes with ammonia, water, and hydrogen fluoride, in which it is an electron donor.

5. The most stable complexes with other hydrides are formed by HF, $H_2O$, and HCl.

6. Judging from the calculated values of the H-bond energy, in practically all these hydrides at least part of the impurity water must be present in the combined state, and the probability of water–hydride molecular complex formation decreases in the order: $HF > NH_3 > HCl > H_2S \cong PH_3$.

In connection with the relative role of specific interactions, it is of interest to compare the energies of the dimers (Table 5) with the effective energies $\varepsilon$ of the paired interactions (Table 2). The difference between these quantities for a given substance are related to two factors: firstly, the quantity $\varepsilon$ includes a contribution from hydrogen bonds, averaged over all nearest neighbours, and not only over those forming bonds; and secondly, the absolute magnitude of the average energy of a hydrogen bond in the condensed phase is lower than that of the energy of the bond in the gas phase. Thus the values of $\varepsilon$ in Table 2 are lower than the values of the energy given in Table 5 for systems with a high hydrogen bond energy, and are close to those for systems with a low bond energy. This comparison for systems for which data are given in both Tables shows that the role of the hydrogen bond is a minimum for phosphine and a maximum for water.

Calculations of the energies of the molecular complexes formed by various hydrides with carbon dioxide, carbon monoxide, nitrogen, fluorine, and sulphur dioxide have been published.[94–100]

To estimate the efficiency of the extensive purification of such strongly polar hydrides as water and ammonia, it is important to have information on the IMI in the complexes with the ions of the elements of groups Ia and IIa, and also with the molecules of the halides of these elements. Data on these complexes have been published;[101–105] their stabilisation energy is several tens kcal mole$^{-1}$.

In Refs.106–109 it was shown for the first time by a non-empirical method in an expanded basis set that many of the hydrides examined in the present review form EDA complexes with the neutral atoms of the metals of the groups Ia–IIIa, and that the latter act as electron acceptors. The formation of associates of this kind must apparently be taken into account in the examination of: a) the contaminating effect of the apparatus (hydride–surface interaction); b) the state of suspended particles in hydrides; and c) the preparation of highly pure elements by the thermal or photochemical decomposition of the volatile hydrides.

The above results of non-empirical quantum-chemical calculations for dimers and heterodimers based on various volatile hydrides make it possible to estimate their stability in the sense of the IMI energy in the ideal-gas state. For the theory of the preparation of highly pure materials, however, it is no less important to have information on the ability of these complexes to dissociate at the temperature of the separation process, characterised by the Gibbs free energy. The processes of complex formation described by Eqn.(6) are generally accompanied by a decrease in entropy. Thus for weak IMI at comparatively high temperatures, the entropy factor may play an important role in the formation of molecular complexes, and conclusions about their stability based only on the values of $\Delta E$ (the enthalpy of formation) may generally speaking be incorrect. The thermodynamic stabilities of weak molecular complexes, based on theoretically determined $\Delta E$ values, have been analysed in a series of papers,[110–113] where the values of $\Delta G_T^0$ were calculated for the formation of the H-complexes $H_2O-HF$, $H_2O-H_2O$, HF–HF, HF–HCl, HCl–HCl, $CO_2-HF$, $Si(OH)_4-H_2O$, and $(H_3Si)_2O-H_2O$ at temperatures of 100, 298.2, and 500 K.

Thus present-day methods of quantum chemistry make it possible to obtain comparatively reliable data on the stability of weak molecular complexes of different types, including those formed by the volatile hydrides of the elements of the second and third periods in the gas phase or in a non-polar solvent. In the study of the same processes of complex formation in polar media, and processes involving molecules formed by the elements of lower periods, experiment provides the only source of reliable information at present.

## VI. THE INTERACTION POTENTIALS OF SYSTEMS WITH MOLECULAR COMPLEXES AND THE RESULTS OF THEIR STUDY BY NUMERICAL EXPERIMENT METHODS

The problem of selecting optimum potential functions, whose components would have a rigorous physical significance, to describe interactions with a specific contribution has not yet been solved. Various versions of paired potentials are used: atom–atom potentials and their extentions, namely site–site potentials, and combinations of spherically symmetrical and non-central compounds. The most systematic models, however, are apparently those in which the contributions of specific and van der Waals interactions are separated:[114]

$$U_N = \sum_{i<j} \{\Phi_{ij} + B(ij)\,u(ij)\} \qquad (12)$$

Here, $\Phi_{ij}$ is the potential energy of the paired-additive interaction of the molecule, characterising the non-specific interactions (for example the Lennard-Jones potential); $u(ij)$ the energy of the donor–acceptor interactions; and $B(ij)$ the characteristic function of bond formation between the given molecules $i$, $j$, equal to unit if a saturated (specific) interaction is localised between the molecules, and otherwise equal to zero.

Various interaction potential parametrisation methods are used. The first, traditional method uses an empirical paired potential, whose parameters are determined from the

condition for the minimum mean-square deviation of the calculated from the experimental values of some characteristic. For a system with hydrogen bonds, this empirical potential is a combination of Lennard-Jones and Coulomb terms and a Morse function, which is assumed (see for example Ref.115) to describe effectively the contribution made by charge transfer to the total energy of the H-bond. A large number of other empirical potentials, of simpler form, for calculating the IMI energy in liquids with weak hydrogen bonds are known.[116] In this traditional approach for dilute solutions, the separation of the contribution of donor–acceptor interactions has been used[117,118] to calculate the distribution coefficient in solutions of various volatile hydrides (see section III). In this method, the components describing the non-specific and weak specific interactions are separated in the parameter $\varepsilon$ of the Lennard-Jones potential (1). For hydrogen sulphide it was found[117] that the contribution of hydrogen bonds to the depth of the potential well (see Table 2) is 60–70 cal mole$^{-1}$. The estimated non-specific component for water, 360–480 cal mole$^{-1}$,[118] also agrees with published data.[119]

Care must be taken, however, when using these parametrisation methods. For example, a calculation of the structure of liquid ammonia using a model potential whose parameters were obtained from data on the second virial coefficient[120] showed the complete absence of any association in the liquid, contrary to experimental data.

A second method of IMI potential parametrisation is based on the results of non-empirical quantum-chemical calculations. In recent years it has become possible to determine comparatively rapidly the energy of dimers at different points of configuration space, that is to obtain fairly complete information on the potential energy surface of the interacting molecules. The parameters of the analytical expressions for the paired potential functions (usually in the form of the sum of the electrostatic and atom–atom contributions) are selected to reproduce most effectively the calculated potential surface.

The IMI potential constructed using the approximate first method or the more accurate second method is then used for a statistical-thermodynamic calculation of the structure and characteristics of pure liquids and solutions with donor–acceptor interactions.

Promising possibilities for practical application to the calculation of the structure and properties of systems with both van der Waals and donor–acceptor interactions are provided by the methods of computational physics: the method of molecular dynamics (MD) [121] and the Monte Carlo (MC) method[122] (see also the published monographs[123,124] and reviews[125,126]). These methods are well known, and will not be described here. It may be noted, however, that algorithms for calculating[127,128] thermodynamic quantities, including the entropy component, for systems with specific interactions have apparently not yet been developed. For these systems, quantities such as the pressure (density), energy, heat capacity, and structural characteristics are calculated.

The principal results of the study of the structural and thermodynamic properties of various liquid hydrides of the elements of the second and third periods with weak specific interactions by numerical experiment methods using rigorous quantum-chemical IMI potentials can be examined.

*Water.* The familiar exceptional chemical and biological importance of water is responsible for the vast amount of published information on various properties of this most widely encountered associated liquid (see for example the published reviews[38,130–132]). The preparation of highly pure water[133] and, on the other hand, as noted repeatedly above, the removal of traces of water from various inorganic and organic materials, are extremely urgent problems. It is in the case of aqueous systems, whose properties are determined to a large extent by comparatively strong intermolecular H-bonds, that the methods usually employed to calculate the distribution coefficient[5–7] and the solubility[134] do not give the desired results.

In pioneering work by Clementi and co-workers,[135] 216 different geometries of the $(H_2O)_2$ dimer, corresponding to four types of configuration, were calculated in an almost Hartree-Fock basis set. The results were approximated by a fairly cumbersome expression consisting of the sum of 16 paired contributions, nine of which describe the electrostatic interaction between the hydrogen atoms and the lone pairs of electrons of the oxygen atoms, while the others describe the attraction and repulsion between the oxygen and hydrogen

**Table 6.** Thermodynamic functions of liquid hydrides from the results of computer experiments using non-empirical potentials.

| Hydride | Calculation method, ensemble | Basis set | $N$ | $T$, K | $E$ | $C$ | $\Delta E_{vol}$ | Experiment | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $E_v$ | $C_v$ | $C_p$ | $E_{vol}$ |
| $H_2O$ | MC, (NVT) (Ref.75) | SCF CI | 343 | 298 | −6.8±0.2 | 13.5±2 | — | −8.1 | 17.9 | 18.1 | — |
| | MC, (NPT) (Ref.129) | SCF CI | 100 | 298 | −7.1±0.3 | 20.6±7 | | | | | |
| | MC, (NVT) (Ref.143) | STO-3G | 125 | 298 | −6.6 | 12.7 | | | | | |
| HF | MC, (NVT) (Refs.144, 145) | STO-3G | 108 | 273 | −4.33 | 17.1 | 5.46 | — | ≤17 | — | 6.7 |
| | | 6-31G | 108 | 273 | −5.62 | 11.8 | 6.85 | | | | |
| | MD, (NPT) (Refs.146–147) | SCF | 216 | 278 | −3.97 | 14.3 | 5.2 | | | | |
| HCl | MD, (NVT) (Ref.150) | 4-31G | 216 | 296 | −2.28 | — | | −2.48 | | | |
| | MD, (NVT) (Ref.154) | SCF CI | 216 | 304 | −2.33 | 8.4 | | | 7.3 | | |
| $NH_3$ | MC, (NVT) (Ref.156) | STO-3G | 128 | 239.7 | −3.05 | 13.3 | 4.88 | −3.75 | 12.7 | — | 5.58 |
| | MD, (NVT) (Ref.157) | SCF | 108 | 269.6 | −5.2 | — | | | | | |

Notation: $E$ is the internal energy, kcal mole$^{-1}$ ($E_v$ in an NVT ensemble, and $E_p$ in an NPT ensemble); $C$ the heat capacity, kcal mole$^{-1}$ K$^{-1}$ ($C_v$ in an NVT ensemble, and $C_p$ in an NPT ensemble); $N$ is the number of particles.

atoms, due to non-electrostatic forces. The potential found in this way was used to calculate the structure of liquid water in an isochoric–isothermal ensemble (NVT ensemble).

The thermodynamic functions of liquid water (Table 6) show good agreement with experiment. A calculation[129] of the thermodynamics of liquid water in an isobaric–isothermal ensemble (NPT ensemble, see Table 6) using the Clementi potential gave good agreement with published data.[135]

The Clementi potential,[75,135,136,141] obtained on the basis of rigorous non-empirical calculations with allowance for CI, is still the best for the theoretical determination of the structure and properties of liquid water, although a number of other potentials, which give sufficient accuracy when used in calculations, were later proposed.[137–140]

On the other hand, a number of authors have studied the possibility of using minimum and restricted basis sets to construct the IMI potentials of associated liquids. The most fruitful results using this approach have been obtained by Jorgensen.[141–145] The potential surface of the water dimer was calculated[142] in an STO-3G minimum basis set (291 configurations) and approximated by a 12-6-3 potential:

$$U = \sum_{i<j}^{N} \frac{q_i q_j}{r_{ij}} + \sum_{\mu,\nu} \left( \frac{b_{mn}}{r_{\mu\nu}^3} + \frac{c_{mn}}{r_{\mu\nu}^6} + \frac{d_{mn}}{r_{\mu\nu}^{12}} \right) \qquad (13)$$

The first term takes account of the long-range electrostatic interaction between four point charges, and the summation is carried out over all pairs of charges belonging to N monomeric molecules. The second sum is taken for all pairs of atoms $\mu$, $\nu$ of type $m$ (O atom) and $n$ (H atom). Liquid water has been modelled by the MC method using potential (13).[143] The data in Table 6 show that the thermodynamic functions of water obtained by Jorgensen by much less laborious calculations also show good agreement with experiment and with Clementi's data.

*Hydrogen fluoride.* A potential of type (13) has also been used to model liquid HF by the MC method.[144,145] The potential surface of the dimer $(HF)_2$ was found in a 6-31G basis set for 250 configurations[144] and in an STO-3G minimum basis set for 285 configurations. An analysis of the calculated atom–atom distribution functions showed that liquid hydrogen fluoride consists of long highly bent chains of molecules (in the solid and gas phases, on the other hand, the chains are linear).

The structure and properties of liquid HF have been studied by the MD method.[146,147] The potential was constructed using the results of calculations of the potential surface of the dimer $(HF)_2$ in an almost Hartree–Fock basis set.[148] The radial distribution functions $g_{FF}$, $g_{HH}$, and $g_{FH}$ and various equilibrium and non-equilibrium properties of liquid HF were calculated (see Table 6).

The main conclusion about the structure of liquid hydrogen fluoride, reached in the works cited, agree with Jorgensen's conclusions,[145] but the first peak of the function $g_{FF}$ in Ref.147 was found to be split into two, and the second and third peaks of all the radial functions were broadened considerably, which does not agree with the fairly high structural order of liquid HF beyond the first coordination sphere. These anomalies are possibly related to the neglect of many-particle interaction, whose contribution reaches 10% of the total energy. The potential of the HF–HF intermolecular interaction has also been obtained.[149]

*Hydrogen chloride.* It follows from what was said above that the ability of HCl molecule to form intermolecular H-bonds is weaker than that of water and hydrogen fluoride. Computer modelling of liquid hydrogen fluoride has been carried out using quantum-chemical potentials.[150–154] In Refs.150 and 151, liquid HCl was studied by the MD method using several potentials which approximated the potential surface of the $(HCl)_2$ dimer, calculated in a 4-31G basis set. The best agreement with experiment (Table 6) was obtained using the potential from Refs.146 and 147. According to these data, hydrogen chloride is a weakly associated liquid, in which chains are formed to a smaller extent than in HF.

In Ref.154, liquid HCl was modelled by the MD method using a paired potential obtained by calculating the IMI in the dimer in an expanded basis set. The second virial coefficient of gaseous HCl and the atom–atom radial functions of liquid hydrogen chloride and some of its thermodynamic functions were calculated (Table 6). The experimental and calculated heat capacities of liquid HCl showed good agreement. In a preliminary report[155] a potential was proposed for the description of hydrogen chloride, including Lennard-Jones, dipole, and quadrupole components, and also polarisation terms. This gave a good description of the structure of the dimers in the gas phase and the structure of the liquid and the solid.

*Ammonia.* The dimerisation energies of various hydrides, given in Table 1, indicate that the tendency of ammonia to form H-bonded dimers is intermediate between those of water and hydrogen chloride. The potential surface of the $(NH_3)_2$ dimer has been calculated[156] in an STO-3G basis set (250 configurations). The results were described by a 12-6-3-1 potential (13), which was subsequently used to model the liquid by the MC method. The structural and thermodynamic data obtained in this way, however, showed insufficiently good agreement with experimental data (see Table 6). The agreement was much better when the modified potential (13) was used.

Various properties of liquid $NH_3$ have been determined by the MD method.[157] The potential surface of the dimer was calculated in an almost Hartree–Fock basis set with allowance for correlation energy (61 configurations). Although the thermodynamic functions found for liquid $NH_3$ showed satisfactory agreement with published data (Table 6), none of the three potentials used[157] made it possible to obtain simultaneously with sufficient accuracy both the thermodynamic functions in Table 6 and the second virial coefficient. The data on the structure of liquid ammonia obtained in Refs.156–158 agree well with one another and indicate only weak (compared with HF and $H_2O$) association in the liquid phase.

The use of quantum-chemical potentials in model pure associated inorganic liquids is at present practically limited to the above systems.

*Dilute solutions.* For a wide range of applied problems, including the calculation of the distribution coefficient, it is necessary to have structural and thermodynamic information on solutions of associated liquids, including their dilute solutions. For this it is necessary to carry out a non-empirical calculation of the potential surface of the base–impurity heterodimer. The number of published papers dealing with this topic is fairly small.

Some of these papers deal with aqueous solutions of simple organic molecules, because of the considerable interest in the hydrophobic effect.[159] The water–methane system[129] provides an example. The potential surface of this heterodimer was calculated in a 4-31G basis set for 28 configurations. The IMI paired potential took account of the interaction between the nuclei and the interaction between the lone pair of electrons of the oxygen atom and the hydrogen atoms in the methane molecule. The Clementi potential was used for the potential of the water–water dimer. The MC

method for an NPT ensemble (number of particles 64, $T = 298$ K, 4-31G basis set) was used to determine the partial molar internal energy, equal to $-11 \pm 15$ kcal mole$^{-1}$. The large uncertainty in its calculation is due to the fact that it represents the difference between the two large values of the energy of the solution and the individual components.

The $H_2O-CH_4$ system was also studied[160,161] in an NVT ensemble, where the potential surface was calculated in a 6-31G basis set for 225 configurations. Data have also been published on the quantum-chemical potentials of the water–ethane,[162] water–benzene,[163] and various other systems.

The results examined in this section demonstrate the fruitfulness of the approach to the study of the structure and properties of liquids, which are characterised by more or less strong specific interactions between the molecules, based on computer modelling with the use of non-empirical quantum-mechanical potentials. Two fundamental difficulties are encountered in this approach. The first is that all the calculations assume the paired additivity of the IMI. This is obviously not completely correct, particularly for systems with fairly strong donor–acceptor bonds. This is indicated in Refs.141 and 164–166, where it is pointed out, in particular, that the magnitude of the correction for the three-particle interaction of water molecules may be comparable with that of the correlation energy. On the other hand, other authors[167,168] assume that the non-additivity observed in the H-bonded systems $H_2S-(H_2O)_2$, $(CH_4)_3$, $(NH_3)_3$ does not play a significant role in the calculation of the structure of associated liquids. To some extent, a way out of this position involves the use of data on the properties of condensed systems in the parametrisation of the potential. This makes it possible to take effective account of the role of non-additive interactions.[169]

The other difficulty in obtaining analytical expressions for the potentials from non-empirical calculations is that the results of the latter depend on the basis set chosen. As already noted, the results with the most reliable accuracy are obtained in calculations in almost Hartree–Fock basis sets taking full account of electron correlation. These methods are laborious and expensive, however, so that they can as yet be used only to solve problems of fundamental importance. If however account is taken of the fact that the rate of increase in the efficiency of computers shows no sign of decreasing,[170,171] then in spite of the above difficulties, it can be expected that further progress in the calculation of various parameters characterising the efficiency of the preparation of highly pure associated liquids will in one way or another be related to the approaches examined in this section, based on the methods of quantum chemistry and numerical experiments.

## VII. CHEMICAL METHODS OF PURIFICATION AND THE FORMATION OF MOLECULAR COMPLEXES

The data examined in sections II–VI relate to the formation of weak molecular complexes by the volatile inorganic hydrides of the elements of groups IVa–VIIa. It has been shown that even in this case, appreciable deviations may be expected from the regular relationships familiar from the theory of extensive purification, based on allowance for only non-specific IMI.

At the same time, complex-forming substances giving stable molecular complexes with energies of several tens of kcal mole$^{-1}$, either with impurities or with the main material, have for long been used to separate and purify various compounds. These methods, based on the marked difference in the complex-forming power of the components, represent a form of chemical method for purifying substances.[2,4]

In chemical methods of purification based on the formation of molecular complexes, the separation factor is proportional to the ratio of the equilibrium constants of the processes of complex formation involving the main material and involving the impurity, and is higher, the greater the difference in the complex-forming power of the impurity and the main material with respect to the complex-forming reagent.[2]

Examples of the use of the ability of various hydrides of the elements of groups IIIa, Va, and VIa to form stable EDA complexes with various Lewis acids and bases in the preparation of highly pure materials can be found, for example, in Refs.9–11.

New interest in chemical methods of purification are also being stimulated by work on the preparation of materials for fibre light carriers, where it is necessary to remove one particular impurity which leads to the absorption of electromagnetic radiation in the range of the spectrum where the fundamental mechanisms of absorption make the minimum contribution. To use these methods successfully in practice, it is necessary to carry out a detailed preliminary study (theoretical and experimental) of the processes of molecular complex formation in each specific case. Studies of this kind are also necessary for the development of new methods of reaction gas chromatography, used successfully to analyse highly pure substances.[172]

## VIII. SUMMARY

The material discussed in the present review makes it possible to point out various important problems in the preparation of highly pure substances, whose solution is related to some extent to the problem of molecular complexes. Firstly, the determination of the state of impurities in substances being subjected to extensive purification. Secondly, the theoretical and experimental determination of the parameters characterising the efficiency of extensive purification. Thirdly, the development of methods of extensive purification and analysis using effective complex-forming reagents.

Complete information on the state and behaviour of impurities in a substance being purified would make possible a directed and justified selection of the method of purification. This requires an experimental and theoretical study of the possible formation of molecular complexes both under model conditions (at comparable concentrations of the components or with a slight excess of one of them) and under real conditions (dilute solutions).

High demands are made of experimental methods for studying molecular complexes, particularly at micro-concentrations of one of the components. It is desirable to use methods which simultaneously give information on the quantitative concentration of impurities and on their molecular state (for example infrared spectroscopy). In some cases, useful information on the state of impurities can be obtained by both semi-empirical and non-empirical quantum-chemical calculations. It is difficult to overestimate their role in the study of the structure and properties of molecular liquids with weak specific interactions. The numerical data obtained by these methods are necessary for predicting at a quantitative level the efficiency of two-phase methods of purification in systems of this kind. The fairly fully developed and universal character of many present-day methods in quantum chemistry makes the approaches described in sections V and VI accessible for the solution of practical problems, including those in the field of extensive purification.

The investigation of the chemical form of impurities in a solution of a substance being purified is also important in connection with the use of complex-forming substances as additives to systems in which the distribution coefficient of

an impurity is close to 1. Selective complex formation should probably also be more widely used in the gas-chromatographic analysis of highly pure substances.

The role of molecular complexes in the preparation of highly pure substances has been examined in the present review for the case of the volatile inorganic hydrides of the elements of groups IIIa–VIIa of the second and third periods, which are important compounds in the preparation of highly pure elements and structures based on them. It can be seen from published data, however, that the intermolecular interactions of different strength in hydrides (particularly in the liquid phase), with a few exceptions (boron hydrides, water, ammonia, hydrogen halides) have as yet been insufficiently studied. There are even fewer published data on the hydrides of the elements of the same groups from the fourth, fifth, and sixth periods. With increase in the requirements to be satisfied by the purity of volatile inorganic hydrides, allowance for the influence of the formation of molecular complexes on the efficiency of extensive purification will become even more necessary. This applies particularly to the extensive purification of inorganic chlorides and organometallic compounds, that is substances whose molecules have a much greater tendency to form molecular complexes than most of the hydrides examined in the present review. Thus both theoretical and experimental work on the detailed study of IMI in systems of this kind is extremely urgent. The data obtained will also undoubtedly increase knowledge of the nature of intermolecular interactions as a whole.

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# The Present State and Problems of the Theory of the Kinetics of Electrode Reactions Accompanied by the Adsorption of Inactive Substances and Reagents

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Problems in the theoretical description of the influence of the adsorption of dissolved species on the rates of electrode processes have been discussed. Present-day theories of the mechanism of the interaction between adsorbed species and ionic reagents have been used to develop a general statistical-mechanical approach to the quantitative examination of the macrokinetics of heterogeneous transformations complicated by the adsorption of ionic or dipolar components of the solution, including the adsorption of the reagents themselves.
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## I. INTRODUCTION

The adsorption of both electrochemically inactive substances and reagents has a significant influence on the kinetics of electrode processes. Extensive experimental material has now been accumulated on the influence of the adsorption of electrochemically inactive substances on the kinetics of electrode reactions. A number of papers also discuss the problem of the existence of a stage involving the adsorption of the reacting species themselves (the ions or dipolar molecules of an organic depolariser) in the resulting electrode process.

An extensive literature has been devoted to various theoretical approaches to the description of the influence of surface-active substances (SAS) on the rates of electrochemical reactions. As yet, however, there is no unique method of interpreting experimental data in terms of current theories of the nature of the elementary stage in electrochemical processes and the mechanism of reactions between reagents and adsorbed species. At the same time, the problem of the mechanism of the influence of SAS and the kinetics of the adsorption of reagents on the rates of electrochemical reactions is of fundamental importance. The problem of the influence of SAS is closely related to the development of a scientific basis for improving many processes in electrochemical technology. The mechanism of this influence must be known in order to investigate the factors determining the anti-corrosion, flotation, extraction, and other properties of SAS of practical importance. These factors characterise the efficiency of the application of surface-active substances in chemical engineering, technology, and other fields. Most existing approaches to the above theoretical problems are based on the so-called transition state method, in which the original problem is formulated in a general phenomenological basis. A specific method for examining the kinetics of reactions in an adsorption layer has also been developed, based on the thermodynamic theory of "partial charge transfer".

The importance of allowance for the electrical double layer in the description of the kinetics of electrode processes was first pointed out in 1933 by Frumkin. He introduced into the equation for retarded discharge (the Tafel equation) two, now familiar, corrections corresponding to the physical "renormalisation" of two quantities: the electrode potential $\phi_0$ in the exponent in the Tafel equation and the bulk concentration of the reagent $c_{0X}$. The quantity $\phi_0$ was renormalised to $\phi_0 - \psi_1$, and $c_{0X}$ to $c_{0X} \exp[-z_{0X}F\psi_1/RT]$, where $\psi_1$ is the potential in the plane in which the reacting species is situated, $z_{0X}$ its charge, $F$ the Faraday number, $R$ the gas constant, and $T$ the absolute temperature.

The equation for retarded discharge with Frumkin corrections provides a qualitative explanation of the observed regular features of the kinetics of charge transfer, and in some cases it makes possible a quantitative interpretation of the experimental data (the $\psi_1$-potential is usually identified with the potential of the outer Helmholtz plane). When there is adsorption of ions or surface-active organic substances (SAOS), however, it is difficult to explain the experimental data on the basis of the classical theory of retarded discharge. The influence of the specific adsorption of inorganic ions (chloride, bromide, and iodide) on electrochemical kinetics was first observed by Iofa and co-workers.[1] They detected an appreciable decrease in the overpotential of hydrogen liberation on mercury in the presence of these ions. The simple theory of retarded discharge could not explain these facts.

In 1952, Frumkin[2] proposed the following equation for the magnitude of the current in the presence of SAS

$$i = \text{const} \cdot f(\theta) \cdot \exp\left\{-\frac{\alpha n F(\varphi_0 - \psi_1) + z_{0x}F\psi_1}{RT}\right\} \qquad (1)$$

where $f(\theta)$ is a function of the degree of coverage $\theta$ of the electrode surface by the inhibitor, $n$ the number of electrons transferred in an individual step, and $\alpha$ the electron transfer coefficient. If an equation of the type $k = k_0(1 - \theta) + k_1\theta$ [3,4] is taken for the standard reaction rate constant, then when

the condition $k_0 \gg k_1$ is fulfilled, the dependence of the function $f$ on $\theta$ will have the form $f(\theta) = 1 - \theta$.[5] The existence of this relationship means that, other conditions being equal, the probability of the penetration of the reacting species into an adsorption layer containing SAOS is equal to the fraction $1 - \theta$ of the probability of their penetration into the same layer not containing the organic substance. In the electrochemical literature, this factor corresponding to the inhibition of electrode processes by added SAOS has been called, not very systematically, the "blocking effect" (it is assumed that the adsorbed molecules of the SAOS are segregated on the electrode and that they block a fraction of the surface $\theta$, and that the electrochemical reaction takes place only on the free area of the surface, corresponding to the fraction $1 - \theta$).

The expression $f = (1 - \theta)^b$ has been proposed for the function $f(\theta)$,[6] but the parameter $b$ was not given a clearly defined physical significance. In Ref.7 the function $f(\theta)$ was approximated by an expression of the form $f = \exp(-\Delta U/RT)$, where the quantity $\Delta U$ is related to the additional activation energy in the presence of the SAS (the potential barrier due to the hindered penetration of the reagent species into the compact layer).

Since surface-active halide ions have an extremely marked influence on the liberation of hydrogen, it was suggested[8] that the influence of adsorbed anions is not due to a change in the $\psi_1$-potential (in other words, to the $\psi_1$-effect), but is due to a decrease in the activity coefficient of the activated complex.

It was subsequently shown,[9,10] however, that if this suggestion is correct, hydrogen ions will be adsorbed and accumulate on the electrode surface. This is not observed experimentally, however. To eliminate this contradiction, it was suggested[9] that the coefficient $l (l \ll 1)$ be introduced into the equation for retarded discharge:

$$i = \text{const} \cdot \frac{f_{\text{Ox}} c_{\text{Ox}}}{f_{\neq}} l \cdot \exp\left\{-\frac{(\alpha n - z_0) F\psi_1 + \alpha n F\varphi_0}{RT}\right\}. \qquad (2)$$

This coefficient characterises the degree of inhibition of the transfer of an ion from the bulk of the solution into a surface layer with a much lower dielectric constant. In Eqn.(2), the quantities $f_{0X}$ and $f_{\neq}$ represent the activity coefficients of the discharging species in the initial state in the bulk of the solution and in the intermediate complex, and $c_{0X}$ is the bulk concentration of the reagent.

The introduction of the coefficient $l \ll 1$ means that only a small proportion of hydrogen ions penetrates into the compact layer from which discharge takes place, and that the potential of the outer Helmholtz layer changes little, so that no appreciable adsorption of these ions takes place. The coefficient $l$ has been interpreted quantatively.[11,12] Thus according to Ref.12, it is possible to write for the coefficient $l$ the expression $l = l_0 \cdot \exp(-k_D\theta - 2a\tilde{\gamma}\theta)$, where $k_D$ is a coefficient characterising the decrease in the dielectric constant in the compact layer when a SAS is introduced into the solution, and $\tilde{\gamma}$ a coefficient which corrects for the mutual attraction of the reagent species in the compact layer. The problem of the influence of ions undergoing specific adsorption on the kinetics of electron transfer has been discussed repeatedly in the literature. In a study[13] of the influence of electrochemically inactive anions undergoing specific adsorption on the kinetics of electrode processes, it was assumed that it is possible to use Frumkin's equation, in which the $\psi_1$-potential can be identified with the potential in the plane within the compact part of the double layer in which the activated complex is situated. The charge of the specifically adsorbed ions was assumed[13] to be continuously distributed throughout the inner Helmholtz plane. In Ref.14, account was taken of the discrete nature of the specifically adsorbed charge, and the $\psi_1$-potential was identified with the micro-potential at the point where the centre of the activated complex was localised.

The effects of the discrete character of the charge in the kinetics of electrode processes were dealt with in a paper[15] which derived the dependence of $\lg(k_{q_1}/k_0)$ on $q_1$ (here, $k_{q_1}$ is the charge transfer rate constant for a density of specifically adsorbed ions $q_1$, and $k_0$ the rate constant for $q_1 = 0$). The derivation is analogous to that of the equation for retarded discharge with a correction for the double layer. It was assumed[15] that the plane in which the centres of the reagent ions are situated coincides with the inner Helmholtz plane, and the effect of the discrete character of the charge is taken into account both in the calculation of the activity coefficient of the reagent ion and in the calculation of the free energy of activation. In all the works cited, the dependence of $\lg(k_{q_1}/k_0)$ on $q_1$ is linear, whereas the experimental data, at least for the discharge of the hydrogen ion in the presence of iodide ions, give relationships which deviate considerably from linearity, particularly at high values of $q_1$.

For a more detailed explanation of the experimentally observed effect of a marked decrease in the hydrogen overvoltage in the presence of specifically adsorbed halide ions in terms of statistical thermodynamics, a theory was developed[16-18] on the assumption that associates or ion pairs are formed, including the reagent ions and adsorbed inactive species. The effect of an increase in the rate of electrode processes as a result of the association of the reagents with inert ions, predicted in the works cited, shows qualitative agreement with available experimental data.[19-23]

The study of the effects related to the change in the rate of an electrochemical reaction when an organic substance capable of being adsorbed on an electrode surface is introduced into the solution is of considerable practical and theoretical interest. Many studies, mainly experimental, have been carried out in this field, and the results have been discussed in many monographs and reviews.[24-32] Theoretical aspects of the influence of SAOS on electrochemical kinetics have been dealt with.[33-36] An equation has been obtained[37] for the current density $i$

$$i = \text{const} \cdot \bar{\Phi}(\Gamma) \cdot \exp\left\{-\frac{\alpha n F\varphi_0}{RT} + \bar{\gamma}(\varphi_0 - \varphi_m)^2\right\} \qquad (3)$$

which takes account of the stage involving the adsorption of the organic depolariser. The quantities $\bar{\gamma}$ and $\theta_m$ in Eqn.(3) are empirical constants, and $\bar{\Phi}(\Gamma)$ the familiar Gibbs adsorption ($\Gamma$) function of the surface-active substance. The influence of the nature and degree of coverage of an electrochemically inactive organic adsorbate on the kinetics of an electrode process has been studied.[38]

The state of the theory in 1977 and the mechanisms proposed in the literature at that time for the influence of SAOS on the kinetics of electrode processes have been fairly fully reviewed.[35] Here, therefore, only the most widely encountered recent theories will be briefly discussed.

To construct a theory of the influence of SAOS on the kinetics of electrode processes, it has been assumed[32,38] that as a result of the different reaction conditions on regions of the electrode surface occupied by an adsorbate and on unoccupied regions, the surface becomes non-uniform with respect to the electrochemical process. Assuming that the rate of the electrode process on the surface occupied by the adsorbate is independent of $\theta$, the expression

for the rate constant is written in the form $k = k_0(1 - \hat{c}) + k_1\theta$, where $k_0$ and $k_1$ are the rate constants of the process on the regions formally unoccupied and occupied by the adsorbate respectively. On the basis of the theory of absolute reaction rates, the authors cited[32,38] essentially postulated that the quantities $k_0$ and $k_1$ depend on $\theta$ in different ways. In particular, in the range $\theta < 0.9$ with the condition that the composition of the solution, the positions of the centres of the activated complexes, and the mechanism of retarded discharge remain unchanged, the following expression was proposed for $k$:

$$k = k_0(1-\theta)\cdot\exp(-s_1\theta - s_2\theta^\sigma) \quad (4)$$

where the parameters $s_1$ and $s_2$ characterise the electrostatic, orientational, and dispersion interactions in the adsorption layer, and the parameter $\sigma$ takes account of the dependence of the energy of interaction on the distance between the adsorbed species.

A slightly different approach to the problem of the influence of SAOS on the kinetics of electrochemical processes was proposed in Refs.5 and 35. The authors cited also started from the theory of absolute reaction rates, but made a number of additional assumptions. In particular, in accordance with Refs.9 and 10, they introduced into the expression for the rate constant a coefficient $l \ll 1$, which takes account of the inhibition of the stage of ion transfer from the bulk of the solution into the structured surface layer consisting of molecules of the solvent and the SAOS. They also introduced an additional parameter $r$, equal to the number of solvent molecules displaced from the electrode surface by the activated complex. Assuming that the $\psi_1$-potential and the free energy associated with the change in the dielectric constant in the surface layer are linearly dependent on $\theta$, they obtained the following equation:

$$k = k_0(1-\theta)^r\exp(-s\theta) \quad (5)$$

The coefficient $s$ characterises the properties of the surface layer, and takes account of the possibility of specific interaction between the activated complex and the molecules of the adsorbate, and can take both positive and negative values. A similar equation was obtained in Ref.39. The problem of the influence of SAOS on the kinetics of electrode processes has also been examined in terms of the thermodynamics of surface phases;[40] equations of type (5) were again obtained, and various particular cases analysed.

A common unsatisfactory feature of most published work on the problem being discussed is that no sufficiently convincing theoretical basis has been given for the original relationships used to calculate the rates of electrode reactions in the presence of SAS. The semi-empirical or purely phenomenological equations used for specific calculations are often questionable, and in a number of aspects simply unsatisfactory.

In the present review, particular attention has been paid to the analysis of theoretical studies in which attempts have been made to develop a more correct approach to the quantitative examination of electrochemical processes complicated by adsorption phenomena at the metal–electrolyte solution interface. The estimation of the significance of these studies and the extent to which they correspond to real electrochemical systems starts from the fundamental fact that any adequate theory must be based on a correct statistical analysis of the process of going from the elementary act of charge transfer through the metal–solution interface to the resulting rate of the electrochemical process. Thus from the physical viewpoint, a feature of fundamental importance is that, in accordance with the Franck–Condon principle, electron transfer takes place at fixed values of the coordinates of the "heavy" species (ions, molecules) in the system. In the absence of specific adsorption, this transfer takes place at fixed positions of the ions or dipoles in the electrical double layer and in the solution. When specifically adsorbed ions or dipoles are present, however, this transfer takes place at fixed positions of all other heavy species. At the same time it is obvious that the rate of the overall heterogeneous process is averaged over the different configurations of all the heavy species in the system, that is the local probability of electron transfer must be averaged in accordance with the corresponding distribution function of all the "heavy" species in the system.

Another problem, directly related to the previous one, is associated with taking account of the effects of the discrete character of the ion or dipole charges in the system, including species undergoing specific adsorption at the metal–solution interface. Thus the local electric field acting on the discrete particles (ions, dipoles) close to the interphase boundary, as a result of the polarisation of the boundary by these particles, differs from the average field described by the Maxwell equations for a continuous distribution of dipole moments or free charges. The characteristic relaxation times of the forces of the "intrinsic electrostatic image", that is the redistribution times of the bound charges of the solvent on the interfacial surface (as a result of the polarisation of this surface by species present in the solution) are about $10^{-14}$–$10^{-15}$ s. The characteristic times of many types of electrochemical reaction, however, have orders of magnitude comparable with those of the fluctuational reorientation times of dipolar solvent molecules in the solvation layers of reactant ions ($\sim 10^{-11}$ s), that is they are greater by several powers of ten than the relaxation times of the forces of the "intrinsic electrostatic image". Thus the discrete character of the charged species and dipolar molecules adsorbed at the interface should influence the probability of the elementary act of electrochemical processes. Moreover, since the magnitude of the electric field created by the forces of the "intrinsic electrostatic image" depends to a significant extent on the state of the polarisation of the solvent close to the electrode, it follows that in a quantitative examination of the influence of the electric double layer and the effects of the discrete nature of the charge on the rate of electrode processes, an important role should also be played by a physically adequate description of the spatial non-uniformity and dispersion of the dielectric characteristics of the solvent in the layer next to the electrode.

## II. PHENOMENOLOGICAL APPROACH TO THE DESCRIPTION OF THE INFLUENCE OF ORGANIC SURFACE-ACTANTS ON THE RATE OF THE DISCHARGE STAGE

### 1. The Physical Premises of the Theory

As noted above, the adsorption of organic substances has a significant influence on the rate of charge transfer. This influence is due to a number of factors which in the presence of organic substances lead to changes in the concentration of the reactant species in the layer next to the surface and in the activation energy of the electrode process. Thus for example if the adsorbed molecules of an organic substance are uniformly distributed over the electrode surface and the degree of coverage of the surface by these molecules is $\theta$, then the probability of the introduction of the reactant species into the adsorption layer without allowance for all

other factors will be a fraction 1 − θ of the probability of their introduction into the adsorption layer in the solution in the absence of the added organic substance. Under these conditions, the factor 1 − θ can be related to the change in the configurational entropy of activation $\Delta\Delta S^{\neq}$:

$$1-\theta=\exp(\Delta\Delta S^{\neq}/R)$$

The interactions of the reacting species with the molecules of the SAOS and the solvent are generally different. The difference between the energies of these interactions is an additional (energetic) reason for the change in the surface concentration of reactant species in the presence of SAOS. The replacement of some solvent molecules by SAOS molecules close to the reactant species also leads to a change in the energy of reorganisation of the medium, and this in turn brings about a change in the activation energy of the elementary act of discharge. Finally, the adsorption of an organic substance on an electrode leads to a change in the distribution of the electric field of the double layer. In other words, in the presence of SAOS there is a change in the $\psi_1$-potential at the point where the activated complex is localised. It follows from the theory of retarded discharge that a change in the $\psi_1$-potential influences the rate of an electrode process both as a result of a change in the surface concentration of the reactant species (if they are charged) and as a result of a change in the activation energy (in all cases).

In many published studies, the theoretical examination of the problems of the inhibition of electrode reactions by added SAOS has taken account of the individual factors indicated, or some combination of them, with the introduction of appropriate corrections into the final equation of the theory of retarded discharge.

Thus the following equations have been obtained, reflecting the dependence on θ of the ratio $i_\theta/i_{\theta=0}$ where $i_\theta$ and $i_{\theta=0}$ are the current densities of the discharge stage at degrees of coverage of the surface by the SAOS of θ and θ = 0 respectively:

$$i_\theta/i_{\theta=0}=1-\theta \qquad [3—4]$$

$$i_\theta/i_{\theta=0}=(1-\theta)\exp(-s\theta) \qquad [5]$$

$$i_\theta/i_{\theta=0}=(1-\theta)\exp(-s_1\theta-s_2\theta^\sigma) \qquad [38]$$

$$i_\theta/i_{\theta=0}=(1-\theta)^r \qquad [6]$$

$$i_\theta/i_{\theta=0}=(1-\theta)^r\exp(-s\theta) \qquad [35]$$

The inhibition parameters $s$, $s_1$, $s_2$, $\sigma$, and $r$ appearing in these equations in papers by different authors often have a different physical significance, depending on the model used and the assumptions made in the derivation of the equation. To avoid this ambiguity, a different more correct method is used in the present work to derive the fundamental inhibition equation, which does not require the introduction of corrections into the final equation of the theory of retarded discharge and which takes account of the combined adsorption of the reactant substances and the SAOS molecules.

## 2. Derivation of the Fundamental Inhibition Equation

It is assumed that the electrode reaction is the reduction of Ox to Red

$$Ox+ne\rightarrow Red \qquad (6)$$

the rate of which is limited by the discharge stage. Since the current density $i$ is determined by the rate $v$ of reaction (6), it follows from Faraday's law that

$$i=nvF \qquad (7)$$

From the theory of absolute reaction rates, the quantity $v$ can be represented as:

$$v=(kT/h)\varkappa c_{\neq} \qquad (8)$$

Here, $k$ is the Boltzmann constant, $h$ Planck's constant, $\varkappa$ the transmission coefficient, and $c_{\neq}$ the concentration of the activated complex. To use Eqn.(8) for a real electrochemical system in which reaction (6) is taking place, the numerator and denominator are multiplied by the activity coefficient of the activated complex, $\gamma_{\neq}$, and by the activity of the substance Ox in the adsorbed state, $a_{Ox}^{(ads)}$. Substituting the result in Eqn.(7) and taking account of the fact that $c_{\neq}\gamma_{\neq}=a_{\neq}$ gives

$$i=nF\varkappa\frac{kT}{h}\cdot\frac{a_{Ox}^{(ads)}}{\gamma_{\neq}}\cdot\frac{a_{\neq}}{a_{Ox}^{(ads)}} \qquad (9)$$

The theory of absolute reaction rates assumes that equilibrium is established between the original state of the system (the substance Ox in the adsorbed state and $n$ electrons in the metal) and the activated complex. The condition for this equilibrium is given by the expression

$$\bar{\mu}_0^{(ads)}+n\bar{\mu}_e^{(m)}=\bar{\mu}_{\neq}^{(ads)} \qquad (10)$$

relating the electrochemical potentials of the participants. Since the activity of the electrons in the given metal is constant, that is

$$\bar{\mu}_e^{(m)}=\bar{\mu}_e^{0(m)}$$

$$\bar{\mu}_{Ox}^{(ads)}=\bar{\mu}_{Ox}^{0(ads)}+RT\ln a_{Ox}^{(ads)}$$

$$\bar{\mu}_{\neq}^{(ads)}=\bar{\mu}_{\neq}^{0(ads)}+RT\ln a_{\neq}$$

the condition for equilibrium (10) can be rewritten as:

$$-\Delta\bar{G}_{\neq}^0=\bar{\mu}_{Ox}^{0(ads)}+\bar{\mu}_e^{0(m)}-\bar{\mu}_{\neq}^{0(ads)}=RT\ln[a_{\neq}/a_{Ox}^{(ads)}] \qquad (11)$$

where $\bar{\mu}_j^0$ represents the standard electrochemical potentials different components $j$, and $\Delta\bar{G}_{\neq}^0$ the standard electrochemical free energy of activation of process (6). Substituting the ratio $a_{\neq}/a_{Ox}^{(ads)}$ from Eqn.(11) in Eqn.(9) gives

$$i=nF\varkappa\frac{kT}{h}\frac{a_{Ox}^{(ads)}}{\gamma_{\neq}}\exp\left(-\frac{\Delta\bar{G}_{\neq}^0}{RT}\right) \qquad (12)$$

Eqn.(12) is usually the starting point for the derivation of the basic relationships of the theory of retarded discharge. There is lack of agreement among different authors, however, on whether the activation energy $\Delta\bar{G}_{\neq}^0$ contains an electrical component or is determined only by the chemical activation energy. As shown above, the quantity $\Delta\bar{G}_{\neq}^0$ contains both chemical and electrical components.

To use Eqn.(12) it is necessary to obtain explicit expressions for the quantities $\Delta\bar{G}_{\neq}^0$, $a_{Ox}^{(ads)}$, and $\gamma_{\neq}$. The quantity $\Delta\bar{G}_{\neq}^0$ can be calculated using a schematic diagram representing the change in the standard electrochemical free energy of the system along the reaction path (Fig.1). This path, which corresponds to movement along the abscissa, represents provisionally the sequence of states through which the reaction system passes in the course of the reaction described by Eqn.(12).

The initial state *I* corresponds to the component Ox in the volume of the solution and $n$ electrons in the metal; state *II* to the component Ox in the adsorption layer and $n$ electrons in the metal; the state ≠ represents the activated complex (in the adsorption layer); state *III* corresponds to the component Red adsorbed on the electrode; and the final

state *IV* to the same component in the bulk of the solution. It is assumed that the transfer of all $n$ electrons takes place in one elementary act.

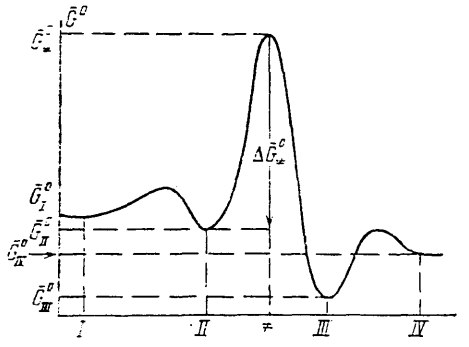


**Figure 1.** Diagram representing the change in the standard electrochemical free energy of a system $\bar{G}^0$ along the reaction path.

Fig.1 shows that $\Delta\bar{G}^0_{\neq} = \bar{G}^0_{\neq} - \bar{G}^0_{II}$. On the other hand, in accordance with Bronsted's principle, several different interpretations of which are possible at present, the standard electrochemical free energy of activation is given by

$$\Delta\bar{G}^0_{\neq} = \Delta\bar{G}^0_{0\neq} + \alpha(\bar{G}^0_{III} - \bar{G}^0_{II}) \qquad (13)$$

where $\alpha$ is the transfer coefficient ($0 \leq \alpha \leq 1$), and the constant $\Delta\bar{G}^0_{0\neq}$ corresponds to the standard free energy of activation with the condition $\bar{G}^0_{II} = \bar{G}^0_{III}$ (see Fig.1).

Analysis of the quantities appearing on the right-hand side of Eqn.(13) shows that the final expression for $\Delta\bar{G}^0_{\neq}$ can be recast in the form

$$\Delta\bar{G}^0_{\neq} = \Delta\bar{G}^0_{0\neq} + \alpha[g_{Ox} - g_{Red} - nF\psi_1 + nF(\varphi_0 - \varphi^0_0)] \qquad (14)$$

where $g_{Ox}$ and $g_{Red}$ are the standard energies of specific adsorption of the species Ox and Red (for positive adsorption, $g_{Ox} > 0$ and $g_{Red} > 0$), and $\phi^0_0$ the standard electrode potential corresponding to reaction (6). Since the standard values of $\Delta\bar{G}^0_{0\neq}$, $g_{Ox}$, $g_{Red}$, and $\phi^0_0$ are independent of the presence of SAOS in the system, it follows that at a given electrode potential ($\phi_0$ = const), the dependence of $\Delta\bar{G}^0_{\neq}$ on $\theta$ is due entirely to the change in the distribution of the electric field in the double layer and is revealed by the corresponding change in the $\psi_1$-potential.

To find the quantities $a_0^{(ads)}$ and $\gamma_{\neq}$ appearing in Eqn.(12), it is assumed that the adsorption of each component of the solution $j$ (except the solvent molecules) is described by isotherms of the form

$$B_j a_j = \frac{\theta_j}{r_j\left(1 - \sum_k \theta_k\right)^{r_j}} \exp\left\{-r_j \sum_k A_{jk}\theta_k + \frac{z_j F\psi_1}{RT}\right\} \qquad (15)$$

Here, $B_j$ is the adsorption equilibrium constant, which depends on the potential; $r_j$ the coefficient of the displacement of the solvent (water) by the component $j$; $A_{jk}$ the constant of the intermolecular interaction between the components $j$ and $k$; and $z_j$ the charge number of the component $j$ (with allowance for the sign).

Eqn.(15) represents a generalised isotherm describing the combined adsorption of both charged and neutral species within one common adsorption layer.

As shown recently,[76] it follows from Eqn.(15) that

$$a_{Ox}^{(ads)} = a_{Ox}\exp\left(\frac{g_{Ox} - z_{Ox}F\psi_1}{RT}\right) \qquad (16)$$

and under conditions in which Ox represents a weakly adsorbed inorganic ion and the solution contains no other surface-active components apart from the SAOS,

$$\gamma_{\neq} = [(1-\theta)^r \exp(rA\theta)]^{-1} \qquad (17)$$

Here, $a_{Ox}$ is the bulk activity of the substance Ox; $r = r_{\neq}$ the coefficient of the displacement of the solvent by the activated complex; $\theta$ the degree of coverage of the surface by the SAOS; and $A$ the constant of the intermolecular interaction between the activated complex and the SAOS molecules.

Substituting Eqns.(14), (16), and (17) in Eqn.(12) gives an expression for the discharge current of reaction (6) in the presence of SAOS:

$$i_\theta = nFk^0_s \cdot \exp\left\{\frac{(1-\alpha)g_{Ox} + \alpha g_{Red} + (\alpha n - z_{Ox})F\psi_{1(\theta)}}{RT}\right\} \times$$
$$\times a_{Ox} \cdot \exp\left[-\frac{\alpha nF(\varphi_0 - \varphi^0_0)}{RT}\right] \cdot (1-\theta)^r \exp(rA\theta) \qquad (18)$$

where $k^0_S = (\kappa kT/h).\exp(-\Delta\bar{G}^0_{0\neq}/RT)$ is the absolute heterogeneous rate constant of the electrochemical reaction.

If the addition of the SAOS does not change the bulk activity of the reaction substance ($a_{Ox}$ = const) and does not change the mechanism of the electrode process ($k^0_S$ = const and $\alpha$ = const), it follows from Eqn.(18) that

$$i_{\theta=0} = nFk^0_s a_{Ox} \cdot \exp\left\{\frac{(1-\alpha)g_{Ox} + \alpha g_{Red} + (\alpha n - z_{Ox})F\psi_{1(\theta=0)} - \alpha nF(\varphi_0 - \varphi^0_0)}{RT}\right\} \qquad (19)$$

Thus for a given $\phi_0$ = const, the following expression is obtained:

$$\frac{i_\theta}{i_{\theta=0}} = (1-\theta)^r \exp\left\{\frac{(\alpha n - z_{Ox})F[\psi_{1(\theta)} - \psi_{1(\theta=0)}]}{RT} + rA\theta\right\} \qquad (20)$$

It is convenient to break down the $\psi_1$-potential into two terms:

$$\psi_1 = \psi_0 + \psi_a \qquad (21)$$

where $\psi_0$ is the potential of the outer Helmholtz plane, which can be calculated from the Gouy–Chapman equation using the experimentally established dependence of the charge on the electrode $q$ on $\theta$. For the quantity $\psi_a$, in a first approximation, a linear dependence on $\theta$ is postulated:

$$\psi_{a(\theta)} = \psi_{a(\theta=0)} - k'\theta \qquad (22)$$

where $k'$ is a constant determined by the position of the activated complex in the compact layer and by the dielectric properties of the latter.

With allowance for Eqns.(21) and (22), Eqn.(20) can be transferred to

$$\frac{i_\theta \cdot \exp[-(\alpha n - z_{Ox})F\psi_{0(\theta)}/RT]}{i_{\theta=0} \cdot \exp[-(\alpha n - z_{Ox})F\psi_{0(\theta=0)}/RT]} = (1-\theta)^r \exp(-s\theta) \qquad (23)$$

where $s$ is the inhibition parameter, equal to

$$s = k'(\alpha n - z_{Ox})F/RT - rA$$

The parameter $s$ reflects both the electrostatic and the "chemical" interaction of the activated complex with the adsorption layer. The other inhibition parameter, $r$, is related to the change in the configurational entropy of

activation $\Delta s^{\neq}$:

$$r \ln(1-\theta) = \Delta(\Delta S^{\neq}/R)$$

Thus examination of the derivation of the fundamental equation of the theory of retarded discharge under the conditions of SAOS adsorption gives Eqn.(23), the right-hand side of which has the form proposed in Ref.35. As shown by the present authors, however, the left-hand side should contain not the usual values of the discharge currents $i_\theta$ and $i_{\theta=0}$ but the corresponding quantities with a correction for the change in the potential of the outer Helmholtz plane in the presence of SAOS. This correction is easily introduced by means of the Gouy–Chapman equation using the experimentally determined dependence of $q$ on $\theta$. Thus for example in the case of a solution containing an excess of a surface-inactive 1,1-valent electrolyte with a concentration $c_{el}$,

$$\psi_0 = (2RT/F)\,\mathrm{arcsh}[q/(8\varepsilon_0\varepsilon RT c_{el})^{1/2}]$$

where $\varepsilon_0$ is the dielectric constant of a vacuum, and $\varepsilon$ the dielectric constant of the solvent.

## III. LOCALISED ADSORPTION OF IONS AND DIPOLAR MOLECULES

In this section, the statistical-mechanical theory of irreversible electrochemical processes complicated by the localised adsorption of inactive ions and molecules is discussed. A central problem in the development of a statistical-mechanical theory describing the influence of SAS on the kinetics of electrochemical processes is the development of an adequate approach to the statistical averaging of the probability of the elementary act of electron transfer over the entire ensemble of "heavy" species in the system. The principles of this approach were described in papers[41,42] dealing with allowance for the influence of the local electric field of the double layer in the equations for the statistical averaging of the probability of the elementary act. In particular, it was shown that the problem of finding the statistically averaged density of the current generated in the elementary act of an electrochemical process can be solved satisfactorily only in two cases: 1) when the electrochemical process does not break down the statistical equilibrium either with respect to the reactants or with respect to the ions of the inactive electrolyte, and 2) when there is no equilibrium with respect to the reacting species, but the reaction takes place in an excess of an electrochemically indifferent electrolyte. The latter should be distributed in space in a quasi-equilibrium fashion, in the sense that its local concentration at each fixed moment of time should be described by the Boltzmann equation, and the magnitude of the field is determined by the instantaneous (not necessarily equilibrium) value of the electrode potential.

The extension of these methods to systems with specific adsorption of ionic and dipolar components of the solution, including the adsorption of reactant species, pointed the way to the development of a quantitative theory of electrochemical kinetics in the presence of SAS.[43–57,60,63,71] This theory takes unified account of inter-particle interaction in an adsorption layer, the influence of the fine structure of the electrical double layer and the influence of the discrete nature of adsorbed ionic or dipolar charges, etc. on the averaged kinetic characteristics of the process.

To illustrate the essential features of the present theory, the irreversible electrochemical reaction of one-electron transfer (6) for $n = 1$, that is the reaction $Ox_z + e \to Red_{z-1}$, where the indices $z$ and $z-1$ of Ox and Red denote the charges of the corresponding ions†, can be considered. It is assumed below that this reaction takes place under conditions in which the centres of specifically adsorbed electrochemically inactive ions are situated within the Helmholtz layer or, more accurately, the reaction layer ($-\beta \leqslant x \leqslant \gamma$ and $\delta = \beta + \gamma$, where $\delta$ is the thickness of this layer).

It will be assumed that the positions of the centres of the adsorbed ions are characterised by the coordinates $\mathbf{r}_1, \ldots, \mathbf{r}_M$ (in the general case, $\mathbf{r}_K$ also denotes all other degrees of freedom of the particles, so that, for example, for dipolar molecules, it includes the orientational and other degrees of freedom of the given particles). The positions of all other species of the solution, including the reactant ions, will be denoted $\mathbf{R}_1, \ldots, \mathbf{R}_N$.

According to the general principles of the theory of the kinetics of heterogeneous processes, the probability $W$ of the elementary act of interphase electron transfer is an exponential function of the activation energy of the process $E_a$:

$$W(\mathbf{R}_1, \ldots, \mathbf{R}_N, \mathbf{r}_1, \ldots, \mathbf{r}_M) = \bar{O}x(\mathbf{R}_1)\cdot\exp(-E_a/kT) \qquad (24)$$

where $\bar{O}x(\mathbf{R}_1)$ is a function which includes the transmission coefficient for the given process. The factor $\bar{O}x = \bar{O}x_z$ is specially distinguished here, since the probability being considered is that of electron transfer to the ion $Ox = Ox_z$ situated at the point $\mathbf{R}_1$, and this factor contains the strongest dependence of $W$ on $\mathbf{R}_1$. The dependence of $E_a$ on the heat of reaction $\Delta I$, however, can be described either strictly quantum-mechanically[58,59] or using the Bronsted relationship. In the general case, the Bronsted relationship is non-linear $E_a = E_a(\Delta I)$, but there is often a linear relationship between $E_a$ and $\Delta I$, that is $E_a = E_a^0 + \alpha\cdot\Delta I$, where $\alpha$ is the transfer coefficient.

From $\Delta I$ it is appropriate to separate the quantity $\Delta I_0$, which is defined by the relationship

$$\Delta I_0(\varphi_0, \mathbf{R}_1) = E_{Ox} - E_m + E_{Red}^{(solv)} - E_{Ox}^{(solv)} + e\varphi_0 + U_{Red}^{(im)}(\mathbf{R}_1) - U_{Ox}^{(im)}(\mathbf{R}_1) \qquad (25)$$

and which takes specific account of the stage of electron transfer from the energy level $E_m$ in the metal to the level $E_{Ox}$ in the ion $Ox = Ox_z$. Thus the total heat of the reaction is written as:

$$\begin{aligned}\Delta I(\mathbf{R}_1, \ldots, \mathbf{R}_N, \mathbf{r}_1, \ldots, \mathbf{r}_M) &= \Delta I_0(\varphi_0, \mathbf{R}_1) + \\ &+ [V_{Red}(\mathbf{R}_1, \ldots, \mathbf{R}_N) - V_{Ox}(\mathbf{R}_1, \ldots, \mathbf{R}_N)] + \\ &+ [\Omega_{Red}(\mathbf{R}_1, \mathbf{r}_1, \ldots, \mathbf{r}_M) - \Omega_{Ox}(\mathbf{R}_1, \mathbf{r}_1, \ldots, \mathbf{r}_M)]\end{aligned} \qquad (26)$$

In Eqns.(25) and (26), the quantities $E_{Red}^{(solv)}$ and $E_{Ox}^{(solv)}$ are the solvation energies of the ions Red and Ox, $\phi_0$ the electrode potential (relative to the bulk of the solution it can be taken as zero), $U_{Red}^{(im)}$ and $U_{Ox}^{(im)}$ the energies of the interactions of the ions Red and Ox with the "electrostatic images" of these ions in the metal and in the electrolyte solution, and $V_{Red}$ and $V_{Ox}$ the energies of the interactions of the ions Red and Ox with the adsorbed ions and the "electrostatic images" of the latter in the metal and solution.

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†Here and subsequently, for uniformity of indexing, this method will be used to represent the reaction which in Refs.43–57 and subsequent papers is represented as $A^z + e \to B^{z-1}$, that is, subsequently, $Ox = Ox_z$ will be written throughout instead of $A^z$, and $Red = Red_{z-1}$ instead of $B^{z-1}$.

The probability of the elementary act $W$ is related to the current density $i$ passing through the system by the expression

$$i = e[\mathrm{Ox}]f\langle W\rangle \qquad (27)$$

where [Ox] is the total number of reactant ions in the solution, and $f = f(\theta)$ a factor which allows for the "effective area" of the electrode surface on which the reaction can take place. The angle brackets denote the operation of statistical averaging of the quantity $W$ over the entire system of "heavy" species present in the solution, including specifically adsorbed species. For the general case of an arbitrary non-linear dependence of $E_a$ on $\Delta I$, the quantity $\langle W\rangle$ is conveniently represented[50] as a contour integral in the complex plane, which in a number of cases is effectively calculated by the method of steepest descent.

It should be emphasised that the averaging of the quantity $W$ depends to a significant extent on the form of the distribution function $D_{N+M}$ of all $N + M$ "heavy" species in the system. At a low concentration of reactant ions, the function $D_{N+M}$ can be written as $D_{N+M} = \Phi_Z(\mathbf{R}_1).D_{N-1,M}$, where $\Phi_Z(\mathbf{R}_1)$ is the one-particle distribution function of the ions $\mathrm{Ox}_Z$, and $D_{N-1,M}$ the distribution function of all other species, with the condition that the reactant ion Ox is situated at the point $\mathbf{R}_1$. The form of the function $D_{N-1,M}$ in turn depends on the nature of the adsorption. The following three physical situations are possible in principle:[50] a) during the characteristic time of the electrochemical reaction, the adsorbed ions remain at the points where they are localised on the electrode surface, that is they act as sources of an additional external field; (b) adsorption is reversible, and in the characteristic time of the electrochemical reaction, equilibrium can be established between the adsorbed ions and the ions in the bulk of the solution; c) in the characteristic time of the electrochemical process, the adsorbed ions are unable to exchange with the ions in the bulk of the solution.

The results for case (a) are given below. In this case

$$\langle W\rangle = \int W(\mathbf{R}_1, \ldots, \mathbf{R}_N, \mathbf{r}_1, \ldots, \mathbf{r}_M)\, D_{N+M}(\mathbf{R}_1, \ldots, \mathbf{R}_N, \mathbf{r}_1, \ldots, \mathbf{r}_M) \times \times \mathrm{d}\mathbf{R}_1 \ldots \mathrm{d}\mathbf{R}_N \qquad (28)$$

and the final result can be represented as

$$i = i_{z-\alpha}(\varphi_0, \theta) \cdot f(\theta) \cdot \exp\{-\Omega_{z-\alpha}(\theta)/kT\} \qquad (29)$$

$$_{-\alpha}(\varphi_0, \theta) = \mathrm{const} \cdot \exp\left\{-\frac{E_a^{(0)} + \alpha e\varphi_0}{kT}\right\} \cdot \exp\left(\frac{\Delta U^{(*)} + F_z - F_{z-\alpha}}{kT}\right) \Phi_{z-\alpha}(x_0) \qquad (30)$$

$$\Omega_{z-\alpha}(\theta) = \frac{e^2 z_0 (z-\alpha)}{\epsilon_{\mathrm{pl}}} \sum_{(m,n)} \int_0^\infty \chi(\lambda) \cdot \exp(-\lambda x_0) \cdot J_0(\lambda R_{mn})\, \mathrm{d}\lambda \qquad (31)$$

here $z_0$ is the charge of the adsorbed ion, $\varepsilon_{\mathrm{pl}}$ the effective dielectric constant of the reaction region, $J_0(x)$ the Bessel unction of the first kind of zeroth order, $R_{mn}$ the distance rom the centre of the ion Ox (in the adsorption plane) to n arbitrary ion having coordinates ($\xi_{mn}$, $\eta_{mn}$) in this lane, $\chi(\lambda)$ a definite function of the integration variable , and the summation is carried out over the entire system adsorbed ions. The plane $x = x_0$ corresponds to the stance of the most probable point for the discharge of the ns from the electrode, and the quantity $\Delta U^{(*)}$ is a mbination of the quantities $U_{\mathrm{Ox}}^{(\mathrm{im})}$ and $U_{\mathrm{Red}}^{(\mathrm{im})}$ at the point . The quantities $F_Z$ and $F_{Z-\alpha}$ are the partial free ergies of the system of ions present in the solution, nus the energy of the interaction of an ion having a harge $ez$ or $e(z - \alpha)$ respectively with the "intrinsic ectrostatic image" in the metal and the solution, $\Phi_{Z-\alpha}(x_0)$ the paired distribution function of the ions; and $\Omega_{Z-\alpha}(\theta)$ e energy of the interaction of the discharging ion with all the adsorbed ions (and their "electrostatic images" in the metal and the solution), which is calculated for the transition state of the discharging ion, characterised by the "effective charge" $e(z - \alpha)$. Under the conditions of the localised adsorption of ions it is necessary to examine in principle both the regular distribution of their adsorption centres (for example the ionic lattice model) and random distribution of the adsorption centres. In a number of cases, the calculations of $\Omega_{z-\alpha}$ are simplified by using the so-called "cut-out disc model"[77] and replacing the summation, for example in Eqn.(31), by integration according to the scheme:

$$\sum_{m,n} J_0(\lambda R_{mn}) \to 2\pi\Gamma_\infty\theta \int_{r_0}^\infty \rho J_0(\lambda\rho)\, \mathrm{d}\rho \qquad (32)$$

where $r_0$ is the radius of the cut-out disc, which depends on the degree of coverage $\theta$, and $\Gamma_\infty$ is the limiting coverage of the adsorption layer. This model is naturally an approximation to the real situation.

A specific calculation based on the above procedure, carried out in Refs.46 and 47, with the condition that there is a linear relationship between $E_a$ and $\Delta I$, gives the following expression for the rate of the electrochemical process:

$$i = \mathrm{const} \cdot f(\theta) \cdot \exp\left\{-\frac{\alpha e[\varphi_0 - \varphi(x_0, \theta)] + \Omega_{z-\alpha}(\theta)}{kT}\right\} \qquad (33)$$

It was assumed that the discharge takes place from the compact part of the electrical double layer, and that the solution contains an excess of a background electrolyte, so that the diffuse character of the double layer can be neglected (the last assumption is more justified, the smaller the ratio $\varepsilon_{\mathrm{pl}}/\varepsilon_0$, where $\varepsilon_0$ is the dielectric constant of the diffuse region of the double layer). In Eqn.(33), $k$ is the Boltzmann constant, and $\phi(x_0, \theta)$ is the potential of the plane in which the ion Ox is situated, and depends on the degree of coverage of the layer $\theta$ by adsorbed ions. The latter are situated in the adsorption plane $x = 0$; ($\xi_{mn}$, $\eta_{mn}$) are the coordinates of the adsorbed ions in this plane.

The physical significance of the quantity $\Omega_{z-\alpha}$ in Eqn.(33) was explained above, and the next task is the specific calculation of this quantity. In Ref.56 it was calculated with allowance for the effect of the penetration of the electric field into the metal (that is the double layer in the metal itself, or in other words the "electron condenser" factor together with the "molecular dipole condenser" in the solution phase of this interphase boundary):

$$\Omega_{z-\alpha}(\theta) = \frac{e^2 z_0 (z-\alpha)}{\epsilon_{\mathrm{pl}}} \cdot \sum_{m,n} \left\{(R_{mn}^2 + x_0^2)^{-1/2} - \right.$$
$$\left. - [R_{mn}^2 + (x_0 - 2\gamma)^2]^{-1/2} - \int_0^\infty \Lambda(x_0, \lambda) \cdot J_0(\lambda, R_{mn})\, \mathrm{d}\lambda\right\} \qquad (34)$$

Here, $R_{mn} = (\xi_{mn}^2 + \eta_{mn}^2)^{1/2}$, and the function $\Lambda(x_0, \lambda)$ under the integral sign has the form

$$\Lambda(x_0, \lambda) = \frac{[\exp(2\lambda\gamma) - 1] \cdot \{\exp[\lambda(x_0 - 2\gamma)] - \exp(-\lambda x_0)\}}{\left[1 + \left(\frac{2}{\nu} - 1\right) \cdot \exp(2\lambda\delta)\right]} \qquad (35)$$

and

$$\nu = \nu(\lambda) = 1 - (\epsilon_{\mathrm{pl}}\lambda)^{-1} \varepsilon_s (\lambda^2 + \kappa_{\mathrm{m}}^2)^{1/2} \qquad (36)$$

$$\Delta\varphi_s - \kappa_{\mathrm{m}}^2 \phi_s = 0 \qquad (37)$$

In the derivation of Eqns.(34)–(36), the electron density distribution in the region of the metal next to the surface was described in the Thomas–Fermi linear approximation (37); $\varepsilon_S$ is the short-wave ("optical") dielectric constant of the metal, characterising the polarisability of the valence electrons of the ionic core of the metal; $\kappa_{\mathrm{m}}^{-1}$ the Thomas–Fermi length for the electrons of the metal (for

a number of metals, the value of $\varepsilon_s$ is close to 1, and the value of $\kappa_m^{-1}$ is ~1 Å). The Thomas–Fermi distribution of electrons in the metal is the simplest model of the double layer in the metal, but it makes it possible to reveal the principal physical aspects of the phenomenon. A more rigorous but mathematically much more complex approach to this problem involves taking account of collective effects in the shielding, allowance for the discrete nature of the ion charge in the metal itself, and other factors.

In Refs. 46 and 47, the following equation was obtained for calculating the quantity $\Omega_{z-\alpha}$ in Eqn. (33) for the inactive ion adsorption conditions being considered:

$$\Omega_{z-\alpha}(\theta) = \frac{e^2 z_0 (z-\alpha)}{\varepsilon_{pl} x_0} - \frac{e^2 z_0 (z-\alpha)}{\varepsilon_{pl}\delta}\left[\Psi\left(\frac{2\delta - x_0}{2\delta}\right) + \Psi\left(\frac{2\delta + x_0}{2\delta}\right) - \Psi\left(\frac{2\gamma - x_0}{2\delta}\right) - \Psi\left(\frac{2\beta + x_0}{2\delta}\right)\right] + \frac{4e^2 z_0 (z-\alpha)}{\varepsilon_{pl}\delta} \sum_{m,n} \sum_{p=1}^{\infty} \sin\left(\frac{\pi p \beta}{\delta}\right) \cdot \sin\left[\frac{\pi p (x_0 + \beta)}{\delta}\right] \cdot K_0\left(\frac{\pi p}{\delta} R_{mn}\right) \quad (38)$$

Here, $\Psi$ is the Euler psi-function, and $K_0(x)$ the zeroth-order McDonald function, which, as in higher orders, has an exponential asymptote at large values of the argument.

The statistical-mechanical theory developed in Refs. 41 to 47 reveals the mechanism of the influence of the electric field, created by specifically adsorbed ions, on the rate of electrode processes. In Eqn. (38) the local electric field appearing in the statistically averaged probability of electron transfer corresponds to the effective configuration of the ionic components of the solution close to the given reactant ion which would be in equilibrium with the reactant if the charge on the latter were $e(z - \alpha)$. The ion with charge $e(z - \alpha)$ is in a certain sense the analogue of the activated complex appearing in the theory of absolute reaction rates. Contrary to the conclusions of this theory, however, the resulting rate of the electrode process is determined by the local electric potential, and not by the average potential corresponding to continuously distributed ionic charges.

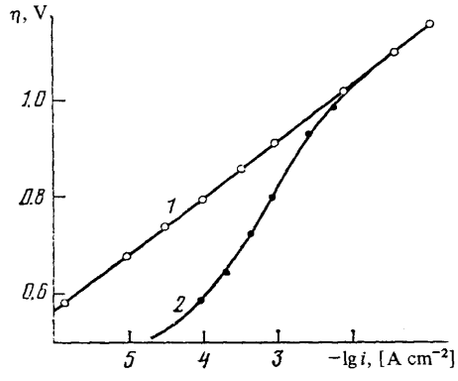



**Figure 2.** Polarisation curves for the discharge of hydrogen ions on mercury from aqueous solutions of 1 M HCl + 2 M KCl (*1*) and 1 M HCl + 2 M KI (*2*); continuous lines—result of the theoretical calculation.[46,47]

In Refs. 46 and 47, the results of calculations based on Eqns. (33) and (38) were used to describe the experimental data from Refs. 1 and 64 on the kinetics of the discharge of hydrogen ions on mercury from mixed aqueous HCl + KCl and HCl + KI solutions. The pre-exponential constant appearing in Eqn. (33) was determined by combining the experimental and theoretical curves in the range of the desorption of the iodide ions. The quantity $x_0$ was used as the fitting parameter of the theory. Quantitative agreement between theory and the experimental data was achieved for the following values of the remaining parameters: $\alpha = 0.5$, $\beta = \gamma = 2.3$ Å, $\Gamma_\infty = 6 \times 10^{14}$ cm$^{-2}$, $\varepsilon_{pl} = 8$, $x_0 = 1.5$ Å (see Fig. 2).

A more detailed analysis of the applicability of Eqns. (33) and (38) for interpreting published data on the influence of the adsorption of ions on the rates of electrochemical reactions were carried out in Refs. 65 and 66. In particular, it was shown that Eqn. (38) gives good agreement between theory and experimental data when the charges on the inactive adsorbed ions and the reactant ions have the same sign. It should be noted, however, that the agreement between theory and experimental data obtained in Refs. 65 and 66 was achieved using additional model representations not present initially in the theoretical equations (33) and (38).

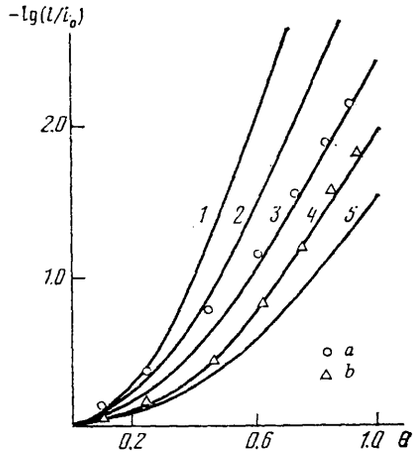



**Figure 3.** Inhibition of the electroreduction of cadmium cations in the presence of t-butylamine (*a*) and t-butyl alcohol (*b*); the continuous lines give the results of the calculation with the following fixed values of the parameters: $\alpha = 0.5$, $\delta = 3$ Å, $\Gamma_\infty = 1.5 \times 10^{14}$ cm$^{-2}$, $x^0 = 1.5$ Å, $z = 2$, $z_0 = 1$, $\varepsilon_{pl} = 8$ and different $x_a = 0.5$, 1.0, 1.5, 2.0, and 2.5 Å (curves *1*–*5* respectively).

Fig. 3 gives the experimental data obtained[67] by measuring the currents for the electrochemical reduction of cadmium cations at a mercury electrode from concentrated aqueous $HClO_4$ solution in the presence of added t-butylamine and t-butyl alcohol. Since these surface-active substances can be adsorbed on mercury from an acidic medium in two forms, neutral and cationic, the rates of the electroreduction were calculated using Eqns. (33) and (38), which take account of the ionic nature of the adsorbed species. Since the theoretical equations contain several parameters for which no reliable experimental values exist (these parameters are, for example $\varepsilon_{pl}$, $\delta$, $\alpha$, $x_0$, $x_a$), the calculations are qualitative. The main aim was to establish the general trend in the influence of cationic SAS in relation to their

position relative to the electrode surface. This problem was solved by constructing a series of curves corresponding to a fixed distance $x_0$ (for constant values of all other parameters of the theory) for varying distances $x_a$. The results of the calculations (see curves *1–5* in Fig. 3) indicate that the inhibition effect increases with decrease in $x_a$. A qualitatively different dependence of the rate of electrolytic reduction on the degree of coverage is observed when the charges on the ions of the adsorbate and the depolariser have different signs.[66,68] This case is examined theoretically in the next section.

The physical principles on which the derivation of Eqn. (33) was based have been used[48,49] to describe the kinetics of electrochemical reactions in the presence of adsorbed inactive dipolar molecules. In the case of the localised adsorption of dipolar molecules, the rate of the electrochemical process is described by Eqn. (39), which is analogous to Eqn. (33):

$$i = i_0(1-\theta)\cdot\exp\left\{\frac{1}{kT}\left[\frac{4\pi e(z-\alpha)\mu x_0\Gamma_\infty\theta}{\epsilon_{pl}\delta} - \Omega_{z-\alpha}(\theta)\right]\right\} \qquad (39)$$

where

$$\Omega_{z-\alpha}(\theta) = \frac{4\pi e(z-\alpha)\mu}{\epsilon_{pl}\delta^2}\sum_{m,n}\cos\sigma_{mn}\sum_{p=1}^{\infty} p\sin\left(\frac{\pi p x_0}{\delta}\right)\times$$
$$\times\cos\left(\frac{\pi p x_a}{\delta}\right)K_0\left(\frac{\pi p}{\delta}\cdot R_{mn}\right) + \frac{4\pi e(z-\alpha)\mu}{\epsilon_{pl}\delta^2}\sum_{m,n}\sin\sigma_{mn}\times$$
$$\times\cos\gamma_{mn}\sum_{p=1}^{\infty} p\cdot\sin\left(\frac{\pi p x_0}{\delta}\right)\cdot\sin\left(\frac{\pi p x_a}{\delta}\right)\cdot K_1\left(\frac{\pi p}{\delta}R_{mn}\right) \qquad (40)$$

The current density $i_0$ corresponds to the absence of adsorbed dipoles. $\mu$ denotes the dipole moment of the adsorbed molecule, and $\mu > 0$ if the dipole is oriented with its negative pole towards the electrode surface; $\sigma_{mn}$ and $\gamma_{mn}$ are the angles characterising the orientation of the dipole with respect to the electrode surface and the reactant ion; and $x_0$ and $x_a$ the positions of the planes in which the centres of the reactant ion and the adsorbed dipoles are localised.

As expected, in the theories adopted for the structure of the adsorption layer, the functional dependence $i(\theta)$ contains in explicit form the values of the angles of orientation of the adsorbed dipoles relative to the electrode surface.[48,49] To determine the influence of the spatial orientation of the adsorbed dipolar molecules on the rate of discharge of the cations, Eqns. (39) and (40) were used to construct two series of curves. The following parameters were unchanged in all the calculations: $\alpha = 0.5$, $\delta = 4$ Å, $x_a = 3$ Å, $x_0 = 2$ Å, $\varepsilon = 8$, $\mu = -1.6$ D, $\Gamma_\infty = 1.5\times10^{14}$ cm$^{-2}$, $z = 2$. Fig. 4*a* gives three curves corresponding to the fixed angle $\sigma_{mn} = 45°$ and three different angles $\gamma_{mn}$: 120°, 90°, and 60° (curves *1*, *2*, and *3* respectively). The influence of the angle $\sigma_{mn}$ (for a fixed angle $\gamma_{mn} = 90°$) is shown in Fig. 4*b*, where curves *1–5* correspond to the angles $\sigma_{mn} = 15°$, 30°, 45°, 60°, and 90°. In the calculation it was assumed that the centres of the adsorbed molecules form a regular two-dimensional hexagonal lattice and that the reactant ion is situated at the centre of an equilateral triangle formed by three adjacent dipoles. Comparison of the two series of curves in Figs. 4*a* and 4*b* shows that the influence of the orientation of the dipoles relative to the reactant ion is stronger than the influence of the angle of inclination to the plane of the electrode.

As in the case of adsorbed inactive ions examined above, the aim of the authors cited[48,49] was not a quantitative comparison of theory with available experimental data (a comparison of this kind has been carried out,[48,51] and gave positive results). It appears much more important and useful to demonstrate the fundamental predictive possibilities of the theory and to analyse the sensitivity of the analytical relationships obtained above to change in the model parameters. The qualitative analysis carried out shows that a satisfactory description of the experimental data can be obtained with completely realistic values of the parameters. In particular, data on the kinetics of the discharge of cadmium and zinc ions in the presence of n-butanol[6,69,70] agree well with the results of a calculation based on Eqns. (39) and (40) and using the values of $\delta$, $\alpha$, $\varepsilon$, $x_0$, and $x_a$ most frequently encountered in the literature for systems of this kind (see Refs. 48 and 51).

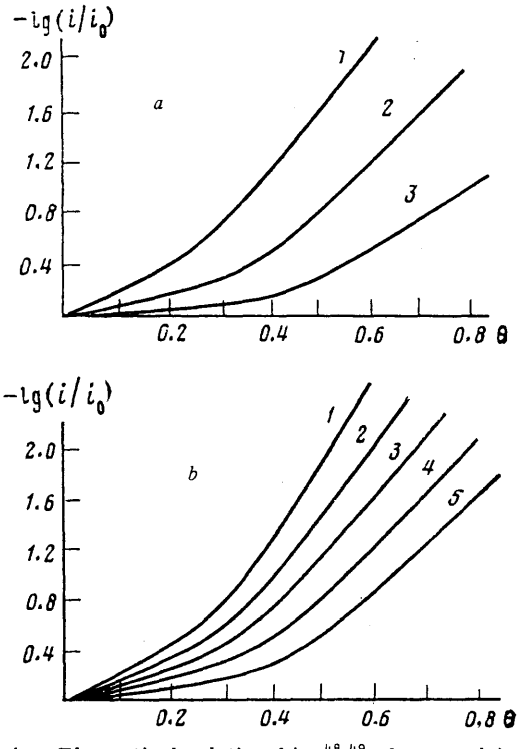



**Figure 4.** Theoretical relationships[48,49] characterising the effect of the inhibition of an electrode process by adsorbed dipolar molecules (the reduction of doubly-charged cations on mercury in the presence of molecules with $\mu = -1.6$ D, oriented mainly with the positive pole towards the electrode): *a*) influence of the orientation of the dipole relative to the reactant ion; *b*) influence of the orientation of the dipole relative to the electrode surface.

Analysis of Eqn. (39) shows that in those cases where the contribution of the interaction described by the term $\Omega_{z-\alpha}(\theta)$ predominates, an increase in the rate of the electrode process by adsorbed SAS is possible.[71] This effect should increase in systems in which the structure of the compact part of the double layer is such that the discharge plane of the ions is situated closer to the poles of the dipoles whose sign is the opposite of that of the charge on the discharging ions. A double-layer structure of this kind is apparently characteristic of the system studied in Ref. 72, where a considerable increase in the rate of the discharge of europium ions on mercury from aqueous N,N-dimethylformamide solutions was observed. A number of other systems in which

the adsorption of organic molecules leads to an increase in the rate of electrochemical processes have been described.[33,73–75]

To explain the experimental data,[72] the authors cited obtained the following equation describing the kinetics of the discharge of the ions $ez$ in this system:

$$i = i_0(1-\theta)\exp\left\{-\frac{e(z-\alpha)\Delta\varphi_{ads}+\Omega_{z-\alpha}(\theta_1,\theta_2)}{kT}\right\} \quad (41)$$

Here, $\theta = \theta_1 + \theta_2$ is the total degree of coverage, and $\Delta\phi_{ads}$ the adsorption potential jump, given by:

$$\Delta\varphi_{ads} = -\frac{4\pi}{\epsilon_{pl}\delta}[\mu_1\Gamma_{1,\infty}(\delta - x_0)\theta_1 - \mu_2\Gamma_{2,\infty}x_0\theta_2] \quad (42)$$

The energy of the electrostatic interaction of the reactant ion in the transition state, corresponding to the charge $e(z-\alpha)$, and the adsorbed species is given by the expression:

$$\Omega_{z-\alpha}(\theta_1,\theta_2) = \frac{4\pi e(z-\alpha)}{\epsilon_{pl}\delta^2}\sum_{p=1}^{\infty} p\cdot\sin\left(\frac{\pi p x_0}{\delta}\right)\left\{\mu_1\cdot\cos\left(\frac{\pi p x_1}{\delta}\right)\sum_{m_1,n_1}K_0\left(\frac{\pi p}{\delta}R_{m_1n_1}\right) + \right.$$
$$\left. + \mu_2\cdot\cos\left(\frac{\pi p x_2}{\delta}\right)\sum_{m_2,n_2}K_0\left(\frac{\pi p}{\delta}R_{m_2n_2}\right)\right\} \quad (43)$$

where the summation with respect to the indices $m_k$, $n_k$ should be carried out in the corresponding adsorption plane ($x = x_1$ or $x = x_2$). With allowance for these results, Eqns.(41)–(43) were used to calculate the dependence of the ratio $i/i_0$ on the relative concentration of the organic phase in the water–organic solvent system.

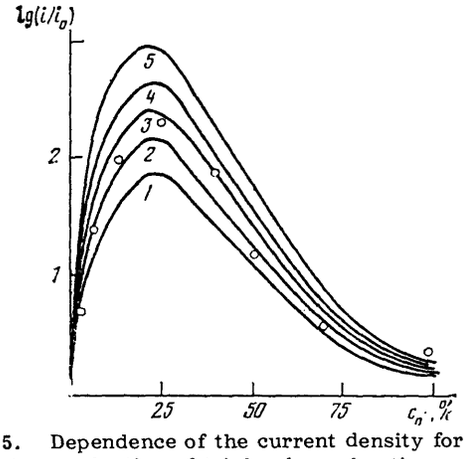



**Figure 5.** Dependence of the current density for the one-electron reduction of triply-charged cations on the relative composition of the mixed solvent, calculated from Eqns.(39) and (40) ($c_0$ is the concentration of the organic solvent); curves *1–3* correspond to values of the dipole moment $\mu$ equal to −2.5, −3.2, −3.9, −4.6, and −5.3 D; the experimental points were taken from Ref.72.

In the calculations it was assumed that in the adsorbed state the dipole moments of the molecules of both solvents are oriented at right angles to the electrode surface (the water molecules with their negative poles towards the electrode, and the organic molecules with their positive poles) and are fixed at the points of a rigid hexagonal lattice. In addition, it was assumed that $\alpha = 0.5$, $x_1 = 1$ Å, $x_0 = 2$ Å, $x_2 = 3$ Å, $\delta = 5$ Å, $\Gamma_{1,\infty} = 5.5 \times 10^{14}$ cm$^{-2}$, $\Gamma_{2,\infty} = 1.2 \times 10^{14}$ cm$^{-2}$, $\mu_2 = 1.8$ D; the value of $\mu_1$ (the dipole moment of the molecule of the organic solvent) was varied from −2.5 D to −5.3 D. The results of the calculations[48,49] are given in Fig.5, which also gives the experimental points obtained for the water–N,N-dimethylformamide system in Ref.72. The simplified character of the picture of the structure of the electrical double layer assumed in the calculations, and the extremely approximate nature of the parameters used, do not provide a basis for a quantitative comparison of the results of the calculation with experimental data. Qualitative agreement can be seen, however, between the theoretical curves in Fig.5 and the experimental data.[72]

The general statistical-mechanical approach described above can be used to calculate the rates of electrochemical processes with allowance for the combined adsorption of several different SAS. Effects of this kind are reflected in the form of the curves giving the dependence of the current density on the degree of coverage.[78] With an adequate quantitative theory, the form of these curves can be used to obtain information on the composition of the adsorption layers next to the electrode.

A method has been proposed[57] for including the effects of the combined adsorption of two surface-active substances in the description of the kinetics of an electrode reaction. A model of the structure of the adsorption layer with two planes ($x = x_1$ and $x = x_2$) in which the centres of the adsorbed species (ions or dipolar molecules) are localised, and a discharge plane $x = x_0$ was examined. This model was used to derive a kinetic equation analogous to Eqn.(41). Cases of the combined adsorption of two different ions or two different dipoles, and also of individual ions with charge $ez_1$, and dipoles (for which the projection of the dipole moment on the perpendicular to the plane of the electrode was $\mu = \mu_1$) were examined. For the last case, in particular, the energy $\Omega_{z-\alpha}(\theta_1, \theta_2)$ is given by the expression:

$$\Omega_{z-\alpha}(\theta_1,\theta_2) = \frac{4\pi e(z-\alpha)\mu}{\epsilon_{pl}\delta^2}\sum_{m_1,n_1}\sum_{p=1}^{\infty} p\cdot\sin\left(\frac{\pi p x_0}{\delta}\right)\cdot\cos\left(\frac{\pi p x_1}{\delta}\right)\cdot K_0\left(\frac{\pi p}{\delta}R_{m_1n_1}\right) +$$
$$+ \frac{4\pi e^2 z_1(z-\alpha)}{\epsilon_{pl}\delta}\sum_{m_2,n_2}\sum_{p=1}^{\infty}\sin\left(\frac{\pi p x_0}{\delta}\right)\cdot\sin\left(\frac{\pi p x_2}{\delta}\right)K_0\left(\frac{\pi p}{\delta}R_{m_2n_2}\right) \quad (44)$$

In the case of the adsorption of two different dipolar molecules with dipole moments $\mu_1$ and $\mu_2$, the corresponding expression for $\Omega_{z-\alpha}(\theta_1, \theta_2)$ has the form (43). To determine the nature of the kinetic curves corresponding to an electrochemical process complicated by the influence of the adsorption of different combinations of SAS, numerical calculations were carried out[57] to determine the dependence of the ratio $i/i_0$ on $\theta$ for the discharge of doubly-charged cations in the presence of two dipolar electrochemically inert SAS, oriented in different ways. The following values were selected for the parameters: $\delta = 5$ Å, $x_0 = 1$ Å, $x_1 = 2$ Å, $x_2 = 3$ Å, $\alpha = 0.5$, $\Gamma_{1,\infty} = \Gamma_{2,\infty} = 1.5 \times 10^{14}$ cm$^{-2}$; the dipole moments $\mu_1$ and $\mu_2$ were assumed to be 1 CGSE unit. The energy $\Omega_{z-\alpha}(\theta_1, \theta_2)$ was calculated from Eqn.(43), but in contrast to the analysis represented by the graphs in Fig.6, the relationship $\theta_1 = f(\theta_2)$ was not determined; it was assumed that $\theta_2 = 1$, and $\theta_1$ was varied. The results of the calculation are given in Fig.6. Qualitative agreement is observed between the calculated graphs for the degree of inhibition and the experimental curves obtained in Ref.78.

## IV. NON-LOCALISED ADSORPTION OF INACTIVE IONS AND MOLECULES AT AN ELECTRODE/SOLUTION INTERFACE

In the examination of the case of the non-localised adsorption of ions and molecules at an electrode/solution interface it is also necessary to carry out statistical averaging of the

probability of the elementary act over the entire ensemble of adsorbed species. A procedure for this averaging has been developed,[52,53] and on the basis of the previously described general approach the authors cited obtained the following expression for the rate of a one-electron reduction:

$$i = \text{const} \cdot (1 - \theta) \cdot \exp\left\{-\frac{\alpha e [\varphi_0 - \varphi(x_0, \theta)] - \Delta F}{kT}\right\} \qquad (45)$$

where $\phi(x_0, \theta)$ is the potential at the point $\xi_0 = \eta_0 = 0$ of the plane $x = x_0$ from which the discharge of the reactant ion takes place, and the quantity $\Delta F = F_z(T, \theta) - F_{z-\alpha}(T, \theta)$ is the difference in the free energies of the system for a charge $ez$ on the ion Ox and an "effective charge" $e(z - \alpha)$ on this ion.

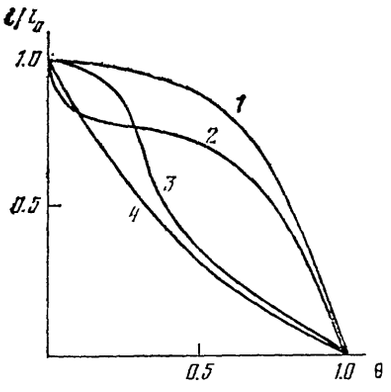



**Figure 6.** Dependence of the current for the electroreduction of doubly-charged cations on the degree of coverage θ under the conditions of the combined adsorption of dipolar molecules of two kinds[57] with the following values of the dipole moments: *1*) $\mu_1 = \mu_2 = 1$; *2*) $\mu_1 = 1$, $\mu_2 = -1$; *3*) $\mu_1 = -1$, $\mu_2 = 1$; *4*) $\mu_1 = \mu_2 = -1$ CGSE unit.

Since $F_z$ and $F_{z-\alpha}$ are related to the corresponding mean-statistical values of $\bar{E}_z$ and $\bar{E}_{z-\alpha}$ of the energies of the system by the Gibbs–Helmholtz thermodynamic relationship, these last quantities are first found by the method of correlative functions (or distribution functions):[79]

$$\frac{\partial \Phi_1(\rho_1)}{\partial \xi_1} + \frac{1}{kT}\frac{\partial U_1(x_0, \rho_1)}{\partial \xi_1}\Phi_1(\rho_1) + \frac{1}{v_s kT}\int \frac{\partial U_2(\rho_1, \rho_2)}{\partial \xi_1}\Phi_2(\rho_1, \rho_2)\,d\rho_2 = 0 \qquad (46)$$

etc., where $\Phi_1$, $\Phi_2$, ... are the unary, binary, etc. distribution functions, $U_1$ and $U_2$ represent respectively the unary and binary (paired) species interaction potentials; and $v_S = \Gamma^{-1} = (\Gamma_\infty \theta)^{-1}$. Relationships (46) represent an infinite system of coupled equations[79] or "chain of equations", and an analogous system of equations is written for the component $\eta_1$ of the two-dimensional vector $\rho_1 = (\xi_1, \eta_1)$ in the adsorption plane $x_a = \text{const}$. The main task is to find an effective method for "terminating" the chain of interrelated equations (46).

Specific results have been obtained[52,53] by introducing "two-dimensional expansions" (with the condition that $\theta < 1$ and that the corresponding integrals converge), that is by expansion of all the distribution functions and thermodynamic quantities being sought in power series with respect to θ; in particular, for $\Delta F(T, \theta)$:

$$\Delta F(T, \theta) = \theta \Delta F_1(T) + \theta^2 \Delta F_2(T) + \ldots \qquad (47)$$

In Eqn.(47), $\Delta F_p$ represents the expansion coefficients which do not depend on θ. For $\Delta F_1$, for example, this method gave the expression

$$\Delta F_1(T) = 2\pi kT\Gamma_\infty \int_0^\infty \{\exp[-U_1^{(z-\alpha)}(x_0, \rho_1)/kT] - \exp[-U_1^{(z)}(x_0, \rho_1)/kT]\}\,\rho_1 d\rho_1 \qquad (48)$$

where $U_1$ is the potential of the interaction of the reactant ion with an arbitrary adsorbed species (with allowance for the interactions of the species with their "electrostatic images" in the metal and the solution). The superscripts on $U_1$ indicate that the reactant ion has the corresponding charge $ez$ or $e(z - \alpha)$.

It follows from Eqns.(47) and (48) that for the non-localised adsorption of the species, the exponent in the expression for the current (45) (with the condition that integral (48) converges) contains a term linear with respect to θ. This is predicted by the theory of the relationship and is apparently reflected in the nature of the behaviour of the experimental $i$, θ curves for systems with adsorption of organic ions.

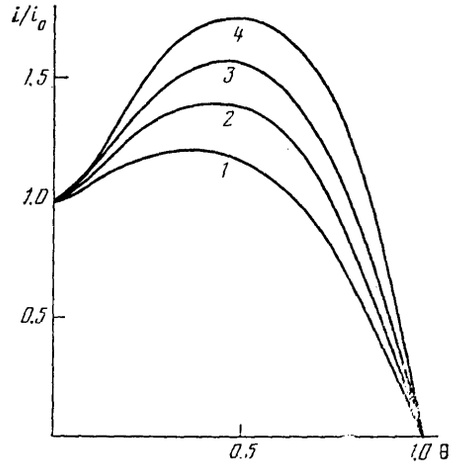



**Figure 7.** Dependence of the current for the electroreduction of doubly-charged cations on the degree of coverage of the electrode surface by inactive singly-charged organic anions.[52,53]

Thus the dependence of the current density on the degree of coverage has been studied[68] under the conditions of the electroreduction of cadmium ions at a mercury electrode in the presence of decyl, nonyl, and octyl sulphate anions. For all the systems studied, the $i$, θ curves show two regions: a region of initial increase and a region of subsequent decrease in the rate of the electrochemical process. According to the theory developed in the present section, these regular features are explained by the different arrangements of the planes in which the centres of the adsorbed ions are localised relative to the plane of the electrode: the closer the localisation of the adsorbed organic anions to the electrode, the more clearly defined the initial region of increase in the current. This effect is illustrated in Fig.7 by four

curves constructed using Eqns.(45)–(48). The common parameters for all four curves were: $z = 2$, $z_0 = -1$, $\alpha = 0.5$, $\varepsilon_{pl} = 8$, $x_0 = 1.5$ Å. The parameters $\Gamma_\infty$ and $x_a$ were varied; curves *1*–*4* in Fig.7 correspond to the following pairs of values of $\Gamma_\infty$ and $x_a$ (in units of $10^{-10}\Gamma_\infty$ and $10^8 x_a$): 4.0 and 2.0 (*1*), 3.0 and 2.5 (*2*), 2.0 and 3.0 (*3*), and 1.0 and 3.5 (*4*). The same trend in the behaviour of the $i$, $\theta$-curves when one organic anion is replaced by another was observed experimentally.[68]

## V. THE INFLUENCE OF THE ADSORPTION OF IONIC REAGENTS ON THE KINETICS OF ELECTROCHEMICAL PROCESSES

A large number of experiments (see for example Refs.9, 10, 29, 32, 33, 80, 81) have established that many electrochemical reactions take place with the reactants in the adsorbed state. The most typical example of reactions of this kind is the discharge of hydrogen ions at a mercury electrode.[1,64] Systems in which even slight adsorption of the reactants can completely change the mechanism of an electrode process have been described. At the same time there have been insufficient quantitative studies of kinetics complicated by adsorption of the reactants. The reason for this is the additional experimental difficulties associated with the need to measure simultaneously, at a given electrode potential, the reaction rate and the concentration of the reacting substance next to the electrode. The first attempts to carry out a theoretical analysis of the influence of adsorption on kinetics were made[33,37] for the reduction of organic substances at a mercury electrode. The analysis was based on the activated-complex method.

A statistical-mechanical approach to the description of the kinetics of electron transfer reactions accompanied by adsorption of the reactants was recently proposed.[53–56] Because of the complexity of the problem, in the initial approximation of the equation for the current $i$ it was assumed that the rate of the process is proportional to the activity $g^*_{ads}$ of the reactant ions in the adsorbed state and the statistically averaged probability $\langle W \rangle$ of the elementary act of electron transfer:

$$i = \text{const} \cdot g^*_{ads} \langle W \rangle \qquad (49)$$

It should be emphasised that completely rigorous and systematic averaging on the right-hand side of Eqn.(49) under the conditions being considered should include the simultaneous determination of both the probability of the given configuration of the system and the probability of the elementary act of the electrode process. This formulation of the problem is extremely complex from both the quantum-mechanical and statistical viewpoints, and its general "analytical" solution (at least without the introduction of any numerically miscalculable model systems) is not yet possible. Eqn.(49) has a factorised (multiplicative) structure, and this is only a definite approximation, whose accuracy cannot be estimated beforehand within a completely rigorous theory.

At the same time, the multiplicative form of the approximation of the equation for the current from Eqn.(49) makes it possible, at least in a whole series of particular cases, to take the solution of this problem to a conclusion.[56] The quantity $g^*_{ads}$ is found from the adsorption isotherms of the species.[53–56] In the works cited, this gave the following equation for the current with adsorption of the ionic depolariser:

$$i = \text{const} \cdot \frac{\theta}{(1-\theta)} \exp\left\{\frac{\mu^{(e)}(\theta) - e[\phi_0 + (z-\alpha)Q(x_1)] - \Omega_{z-\alpha}(\theta)}{kT}\right\} \qquad (50)$$

where the following notation has been introduced:

$$Q(x_1) = \begin{cases} \varphi_0\left(1 - \frac{x_1}{\delta}\right) + \frac{4\pi e z \Gamma_\infty \theta}{\epsilon_{pl}\theta} x_1(\delta - x_0), & \text{for } 0 \leqslant x_1 < x_0 \\ \varphi_0\left(1 - \frac{x_1}{\delta}\right) + \frac{4\pi e z \Gamma_\infty \theta}{\epsilon_{pl}\theta} x_0(\delta - x_1), & \text{for } x_0 \leqslant x_1 \leqslant \delta \end{cases} \qquad (51)$$

Here, $x_0$ is the position of the plane of the adsorption of the reactants in the "inactive adsorbed" state, and $x_1$ the position of the plane from which the discharge of the adsorbed ion takes place; the quantity $\mu^{(e)}(\theta)$ is the electrostatic component of the electrochemical potential of the adsorbed ions. The calculation equations for $\Omega_{z-\alpha}$ are given in the works cited. With allowance for the effect of the penetration of the field into the metal (that is the influence of the "electronic condenser"), it is necessary to modify the quantity $\Omega_{z-\alpha}$ in Eqn.(50) in accordance with Eqns.(34)–(37). Ref.56 also gives an equation for $U_{z,\mu}$, that is the energy of the reaction of the ion with a dipolar molecule with allowance for the penetration of the field into the metal. This quantity is necessary for calculations for conditions in which an organic depolariser is adsorbed.

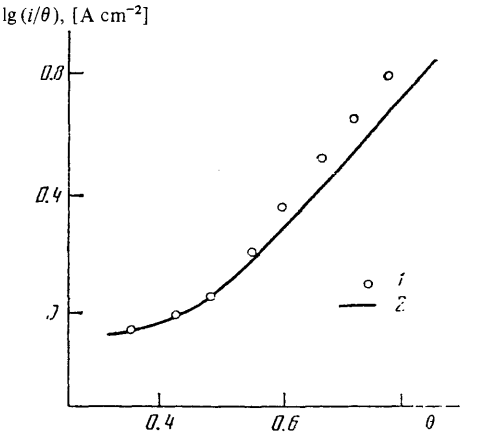



Figure 8. Dependence of the current for the electroreduction of the cationic complex *cis*-Cr(en)(NCS)$^+$ on the degree of coverage of the mercury electrode surface: *1*) experimental points, *2*) results of the calculation using Eqns.(50) and (51).

Eqns.(50) and (51) have been used[55] to calculate the dependence of the current density on the degree of coverage at a constant potential. The numerical values of the parameters were selected for the specific system formed by mercury with the isothiocyanato-complex of chromium *cis*-Cr(en)$_2$(NCS)$_2^+$, where en = ethylenediamine. The kinetics of the discharge of complexes in this system have been studied experimentally.[82] The values of $\Gamma_\infty$ and $\alpha$ measured in this study were $1.5 \times 10^{14}$ cm$^{-2}$ and 0.8 respectively. The following values were taken for the other parameters in the calculations: $\delta = 5$ Å, $x_0 = 3$ Å, $x_1 = 2$ Å, $\varepsilon_{pl} = 6$, $z = 1$. The results of the calculations are compared with the experimental data in Fig.8. It can be seen that at sufficiently low degrees of coverage, the agreement between theory and experiment is satisfactory. The appreciable discrepancy at high degrees of coverage

is apparently related to the fact that at high values of $\theta$ it is not physically justified to regard the discharging complex as a point charge. It would be more adequate to examine the discrete structure of the charges within the actual complex. Another reason for the lack of agreement between the results of the calculation and the experimental data may be the neglect of the contribution from the effects of the penetration of the electric field into the metal, although, as noted above, it is possible in principle to take account of these effects on the basis of the equations given in the present review.

## VI. SUMMARY

Studies directly in the field of the theory of the electrical double layer and the theory of the adsorption of SAS and SAOS on electrodes and also in the field of the theory of the kinetics of electrode processes are now being intensively developed to solve a number of problems in theoretical and applied electrochemistry. These fields of present-day theoretical electrochemistry are organically related and interact naturally with one another, and this interaction process is gradually becoming more interpenetrating and requiring the development of theoretical correlations and self-consistency. An example is provided by the aspects, examined in the present review, of the theory of electrochemical processes complicated by adsorption phenomena at the interface between the electrode and the electrolyte solution.

It should be emphasised that progress in the first two fields naturally provides a basis for the further development of the theory of the kinetics of electrode reactions. In this connection, there is no doubt that recent developments in the theory of the equilibrium double layer, such as the "three state" model or the "cluster" model, the concept of condensed adsorption layers on electrodes with the interpretation of the reorientation of adsorbed molecules as a two-dimensional phase transformation, the representation of two electronic "parts" of the total charge of an electrode (the part of the charge "spread" uniformly over the metal surface and the other part which is the sum of the electronic counter-charges localised close to specifically adsorbed ions) may be reflected in the theory of the kinetics of electrochemical reactions (a bibliography) of relevant work can be found, for example, in a published review).[62]

The present review has dealt partly with the kinetic aspects of the penetration of the electric field into a metal. As has been pointed out,[52] however, it is also necessary to take account of the effect of the shielding of the field of the metal by the "outer" electrons, that is the electrons of the metal penetrating into the effective range of the "compact" layer adjoining the metal (the so-called "electron tails"). These electrons interact with the solvent molecules and adsorbed species, and in this connection it has been emphasised[52] that under these conditions the actual concept of "compact layer" (or "reaction region" in the kinetic aspect) requires physically more correct and electrochemically constructice definitions (concepts), and also definition of the concept of the phase interface (thus for example the theory of the "capacity of the double layer" should include a factor associated with the "electron condenser", etc.).

In addition to these factors, other characteristic features such as the specific structure of the region of the solvent next to the surface (in particular, the influence on its structure of the "outer" electrons of the metal[52] and the possibility in principle of hydrogen bond formation between water molecules in the solvent monolayer [83,84]), the effects of the spatial dispersion of the dielectric constant of the two phases in contact, the questions of "partial charge transfer" in the adsorption of species on electrodes, and a number of other questions will undoubtedly be reflected in the theory of electrode kinetics.

The problem of the statistical averaging of the probability of the elementary act of an electrochemical process accompanied by the adsorption of electrochemically inert species or the reactants themselves was analysed in detail above, and it was shown, in particular, that the interaction between the reactants and adsorbed species is determined by the fine structure of the electrical double layer at the electrode/solution interface. A unique type of electrochemical system is provided by systems in which electrode reactions take place with the reactants in the adsorbed state. In this case, in the averaging of the probability of the elementary act, it is necessary to take into account both the contribution made to the free energy of adsorption of the reactants by the electric field created by these reactants, and the entropy factor, which influences the production of the ionic adsorption isotherm. In the theory of the kinetics of reactions complicated by adsorption, it is also necessary to take account of the structure and parameters of the electronic spectrum of the metals. Thus it is obvious that from the physical viewpoint also, the further development of the theory of the kinetics of electrode reactions complicated by adsorption phenomena at the metal/solution interface is an extremely urgent task.

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# Reactions in Organic Crystals

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Structural studies on the following types of chemical reactions in organic crystals published after 1977 are considered: dimerisation, redimerisation, polymerisation, asymmetric synthesis, chemical reactions in clathrate compounds, topotactic redox reactions in intercalation systems, and crystal-gas reactions. A common feature of all the processes examined is the influence of the crystal environment of the molecules of the initial substance on the mechanism of the reaction and the character of its product (the topochemical factor).
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## I. INTRODUCTION

Solid-phase reactions are attracting increasing attention at the present time for a number of reasons. Firstly, the limited mobility of the reacting molecules in the crystal makes it possible to carry out a well-founded structural investigation of the entire chain of molecular transformations, i.e. of the reaction mechanism. Secondly, with the aid of solid-phase reactions, it is possible to obtain polymers with a regular structure, enantiomerically pure products with the configuration of the chiral centres specified beforehand, large defect-free single crystals, which are especially suitable for electrophysical measurements, etc. All these features have led to the appearance and development of a new field of scientific research—crystal engineering, whose aim is to investigate the principles and rules governing the construction of different types of packing of potentially reactive molecules and crystals such that favourable conditions are created for the involvement of the molecules in particular chemical reactions and rearrangements not requiring diffusion and accompanied by only a slight rearrangement when the process is subject to topochemical control.[1]

This review surveys the principal results of structural studies on chemical reactions in organic crystals published after 1977 and not included in our previous review,[1] which dealt with the intramolecular rearrangements and reactions involving the formation of low-molecular-weight products in the solid phase.

The dimerisation and polymerisation reactions, to which the greatest number of structural investigations have been devoted, are discussed in greatest detail. With the aid of these reactions, it is possible to obtain in some cases the final product in the form of a single crystal, which is nowadays of practical importance.

The reactions in clathrate compounds and topotactic redox reactions in intercalation systems, which are intermediates between topochemical transformations in organic crystals and charge-transfer processes in low-dimensional binary systems, are also fairly close to practical application. However, in view of the limited space available in the review, these processes are considered only briefly, although topochemical analysis of the charge-transfer conditions in organic systems, considered as a solid-phase chemical reaction, is fruitful.

The classification of solid-phase reactions employed in this review is somewhat arbitrary, but it makes it possible to differentiate the main types of processes and the directions of further development of this interesting field at the junction between organic chemistry, crystal chemistry, and physical chemistry.

## II. DIMERISATION

Dimerisation belongs to one of the most thoroughly investigated types of solid-phase chemical reactions. In essence, the strategy used in crystal engineering†[2] has been developed in relation to the solid-phase synthesis of optically active olefin dimers (and polymers)[3-9] by cycloaddition with formation of cyclobutane derivatives.

It has been established that the occurrence of these processes requires the type of packing in the crystal where the reacting double bonds are parallel and separated from one another by not more than 4.1 Å.[2] If these conditions are met, the overall geometry of the atomic environment of the reacting double bonds persists in the cyclobutane product, i.e. these processes are subject to topochemical control.#

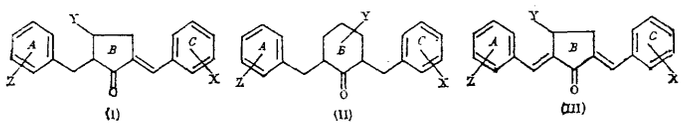
### 1. Benzylidene Derivatives of Cyclopentanones and Cyclohexanones

Compounds based on 2-benzyl-5-benzylidenecyclopentanone (I), 2-benzyl-6-benzylidenecyclohexanone (II), and 2,5-dibenzylidenecyclopentanone (III) are extremely promising for the study of solid-phase dimerisation and topotaxy of crystals as well as crystal engineering. Derivatives of these compounds (substituted in the *A*, *B*, and *C* rings) have been investigated in the dimerisation reaction in the crystalline state under UV irradiation.[11]

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†Solid-phase chemical reactions are controlled by specific types of organisation or by varying the character of the packing in the crystals of the initial compound.

#This rule agrees with a general topochemical principle, according to which reactions in organic crystals proceed with minimal atomic and molecular shifts.[10]



(I) (II) (III)

These systems are of considerable interest, because, in principle, it is possible to follow with their aid the non-diffusional rearrangement of atoms directly in the course of the chemical reaction.[5,12]

Table 1. The capacity for solid-phase dimerisation of the benzylidene derivatives of cyclopentanone and cyclohexanone whose structures have been investigated.[11]

| Compound | X | Y | Z |
|---|---|---|---|
| (Ia)* | H | H | H |
| (Ib) | *p*-Br | H | H |
| (Ic) | *m*-Br | H | H |
| (Id) | *o*-Br | H | H |
| (Ie) | *p*-Cl | H | H |
| (If) | *o*-Cl | H | H |
| (Ig) | *p*-$CH_3$ | H | H |
| (Ih) | *m*-$CH_3$ | H | H |
| (Ii)* | H | H | *p*-Cl |
| (Ik)* | H | H | *p*-$CH_3$ |
| (Il)* | *p*-Br | H | *p*-$CH_3$ |
| (Im) | *p*-Br | H | *p*-Cl |
| (II)* | H | H | H |
| (IIIa)* | H | H | H |
| (IIIb) | H | Me | H |
| (IIIc)* | H | Me | H |

*Has the ability to dimerise.

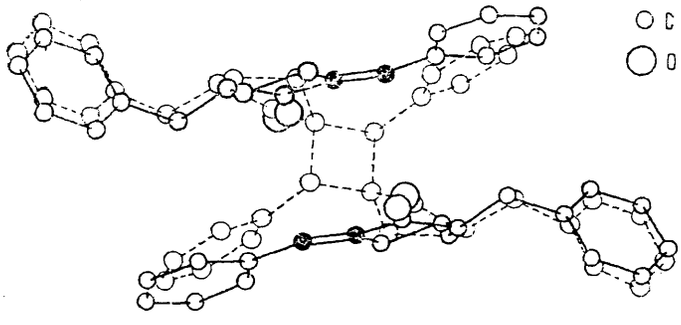



Figure 1. Schematic illustration of the dimerisation of compound (IIa) on irradiation with u.v. light in the crystal. The bold lines represent the monomer molecules and the dashed lines the centrosymmetric dimer molecule; the C atoms linked by a C=C bond are shown shaded. The insignificant shift of the benzene rings on dimerisation is worthy of note.[5]

The majority of reactive compounds of series (I), (II), and (III) (Table 1) crystallise in such a way that the nearest molecules are linked via their centres of symmetry and they therefore form centrosymmetric dimers in the solid-phase reaction (Fig.1). The double bonds in the crystals of compounds (Ia), (Ib), (Ii), and (II), whose structures have been investigated, are separated by distances of 4.2, 3.8, 4.0, and 3.8 Å respectively. The photostability of the remaining series (I) compounds can be accounted for by the larger distance between the double bonds [for example 6.2 and 4.7 Å in the crystal of compound (Ie) for molecules linked by glancing reflection planes]. The crystals of compounds (IIIb) and (IIIc), in which an asymmetric centre arises in the 3-position as a result of the introduction of the methyl substituent into the *B* ring constitutes an exception: the racemate (IIIb) is photostable and the crystals of the individual (IIIc) enantiomers are reactive. In the topotactic dimerisation of compound (Ia) (a single crystal–single crystal transition) the maximum change in the unit cell parameters is 0.7%.[5] However, by controlling carefully the rate of dimerisation, it is possible to achieve a homogeneous single crystal–single crystal transition for compound (Ib) and also for relatively large changes in the unit cell parameters (3.8, 5.6, and 6.5% for periods *a*, *b*, and *c* respectively).

Systems (I)–(III) open up completely new prospects in solid-state chemistry, namely the possibility of investigating the mechanism of a photochemical reaction in the crystal. The first step in this direction was the investigation of the variation of the unit cell parameters with increasing degree of conversion for a crystal of compound (Ia) in which the distance between the reacting double bonds is 4.166 Å, while the distance between the planes in which these bonds are located is 3.80 Å.[11]

The molecules in the crystal (Ii)[13] form around the centres of symmetry predimers in which the distance between the planes incorporating the C=O and C=C double bonds in each molecule is 4.036 Å, as well as the unsubstituted benzene ring. The intermolecular distance between the double bonds in such a predimer (4.027 Å) allows [2 + 2]-cyclodimerisation.[2] For this reason, on photoexcitation, these bonds can interact topochemically to form a cyclobutane ring, which has in fact been observed experimentally.

In order to elucidate the causes of the conversion of compound (II) into an amorphous form in its solid-phase photodimerisation reaction, its crystal structure was determined.[13] The molecules in the crystal of compound (II) also form predimers around the centres of symmetry with a distance of 3.028 Å between the planes incorporating (within each molecule) both double bonds and the unsubstituted benzene ring, which indicates a strong intermolecular interaction between the conjugated π-electron systems of the molecules. The shortest distance between the atoms involved in the C=C double bonds in the predimer is 3.792 Å. The loss of crystallinity by compound (II) as a result of photodimerisation[14] is probably associated with the necessity for an appreciable displacement of the dimer molecules due to the very close relative positions of the molecules in the predimer. In fact, in the crystal of compound (Ib), whose photodimerisation involves a single crystal–single crystal transition, the distance between the planes of the conjugated molecular systems in the predimer is 4.174 Å,[12] which is much greater than in compound (II). Furthermore, the decrease of crystallinity on photodimerisation can be caused by the low melting point of the product. The decrease of the melting point on formation of the new phase can induce the removal of the topochemical control over the solid phase reaction.[15]

Ideas concerning the possibility of topochemical interaction in crystals of types (I)–(III) have been developed[16] from an X-ray diffraction study of compounds (IIIa) and (IIIb) as well as the product of the solid-phase dimerisation of compound (IIIa).

The reactive C=C bonds of the neighbouring molecules in the photoactive crystal of compound (IIIa) and in the photostable crystal of compound (IIIb) have approached one another to distances of 3.720 and 3.871 Å respectively, permitting a topochemical interaction. However, these bonds

are not parallel, i.e. the condition necessary for topochemical interaction is infringed.[2,10,17] Nevertheless, photochemical dimerisation is observed in the crystal of compound (IIIa). The explanation is that, despite the lack of a parallel arrangement of the reacting double bonds (they form an angle of 56°), the axes of the $p_z$ orbitals of the carbon atoms in compound (IIIa) are parallel. This is not observed in the crystal of compound (IIIb), which accounts for its photostability.

According to X-ray diffraction data,[16] the dimerisation of compound (IIIa) leads to the formation of precisely the isomer which should be obtained, i.e. the topochemical reaction proceeds via a defect-free mechanism. However, in contrast to the dimerisation of compound (Ia), the crystal structure of compound (IIIa) breaks down as a result of dimerisation and an amorphous product is formed. The transition to the amorphous state can be caused by the greater rigidity of the molecule of compound (IIIa) [i.e. its smaller ability, compared with compound (Ia), to "become adjusted" to the lattice of the new phase] and also by the necessity for the rotation of the molecules of compound (IIIa), because the formation of the dimer still requires that the double bonds of the interacting molecules be parallel.

The phenomenon of "structural mimicry" (the ability of molecules to change their conformation on becoming incorporated in the crystal lattice of the "host") has been used successfully[18] to ensure the reactivity of compound (Im), which is inert in the crystalline state, as a result of the formation of its solid solution with the reactive compound (II). The molecules of compound (II) have a planar conformation in the crystal, while those of compound (Im) have a bent conformation. This difference between the conformations, caused by the electronic and steric influence of the chloro-substituent,[18] changes the character of the molecular packing in these crystals. The mixed crystal having the composition (II) : (Im) = 7 : 3 is isostructural with the crystal of compound (II) and is photoactive, while the disposition of the double bonds satisfies the conditions for topochemical dimerisation. Whereas the distance between the double bonds in the photostable crystal of compound (Im) is 4.65 Å, in the photoactive crystal of compound (II) the C=C bonds of the molecules, linked via the centre of symmetry, are parallel and separated by 3.92 Å. In the mixed crystal the molecules of compound (Im) are forced to assume an extended conformation and the distance between the C=C bonds diminishes to 3.87 Å.[18] Thus Jones et al.[18] expanded the range of available tools in crystal engineering, previously restricted to the use of various "controlling" groups,[2,3,6,19] having used "structural mimicry" to convert the inactive molecules into a reactive form (conformation) by distributing them within a specified "active" packing.

## 2. Cyclohexylidenephenyl-5(4*H*)-oxazolones

In the course of the solid-phase photolysis of cyclohexylidenephenyl-5(4*H*)-oxazolones (IV), asymmetric dimers of three types, (V)–(VII), are formed.[20–23]

The structures of compounds of type (IV) with X = H[21] and Cl[22] the crystals are isomorphous), (V) (colourless main product with X = Cl[21]), and (VI) (yellow main product with X = H[20]) have been determined.

The crystal of compound (IV) has a layer structure with shortened distances between the molecules linked via the glancing reflection plane *b* (space group *Pbcn*). The formation of trispiropyrroloisoquinoline (V) in the crystal of compound (IV) not only as a result of asymmetric dimerisation but also due to the formation of two new C–N and C–C bonds between neighbouring molecules requires the transfer of one of the hydrogen atoms of the benzene ring to the nitrogen atom and the formation of a C–C bond between the benzene and cyclohexane rings. The geometry and relative orientations of the molecules in the predimer (IV) favour such a rearrangement.[21]

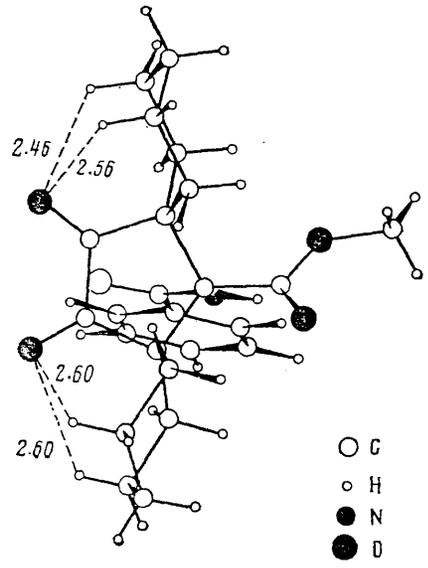
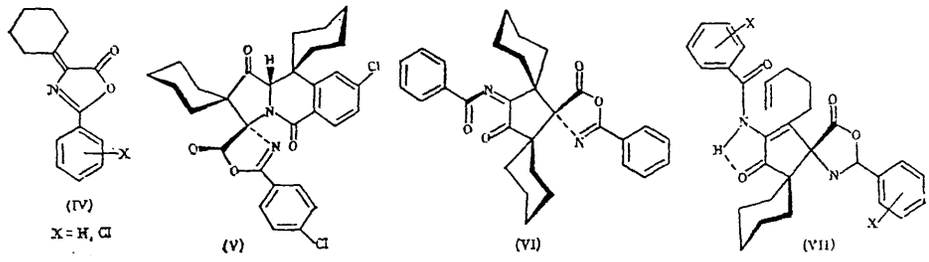
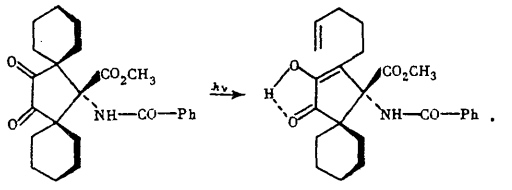



Figure 2. The structure of the diketoester (VIII) molecule. The short γ-H...O contacts are indicated by dashed lines.[20]

The formation of a dimer of type (VI) can be formally represented as asymmetric ($\pi^2 + \pi^2 + \pi^2 + \sigma^2$)-dimerisation of two molecules of the oxazolone (IV) linked by the plane *b*. The dimer having the presumed structure (VII) is not the primary solid-phase dimerisation product but is formed from the yellow dimer (VI) as a result of a Norrish fragmentation of the second type[20] with transfer of a H atom to the N atom.



Specific hypotheses concerning the mechanism of the γ-H transition are difficult to formulate in view of the disordered nature of the structure of compound (VI) in the region where the *N*-benzoylimino-group is located. However, fragmentation of the second type is characteristic not only of *N*-benzoyl-1,2-diketoimine (VI) but also of dispiro[5,1,5,2]pentadecane-14,15-diones obtained from the dimer (VI, X = H). For example, the yellow diketoester (VIII) gives rise to the colourless fragmentation product (IX).

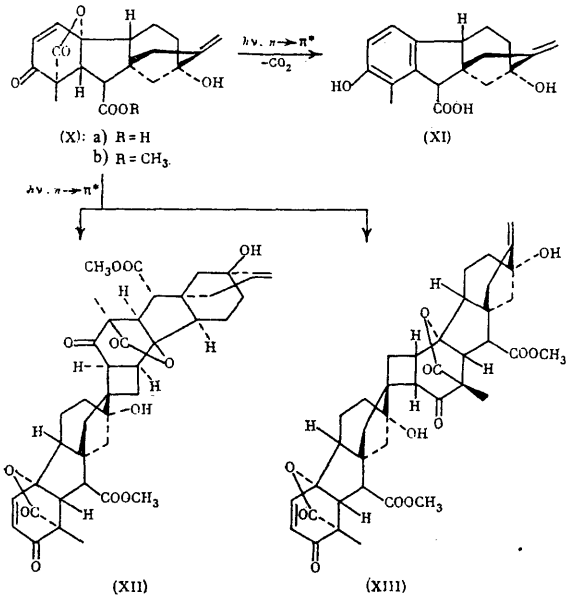


(VIII) (IX)

In the crystal of compound (VIII)[20] the four axial γ-hydrogen atoms are involved in intramolecular contact with the corresponding oxygen atoms of the keto-groups over distances of 2.46–2.60 Å, which favour the interaction (Fig. 2).

### 3. Derivatives of 3-Dehydrogibberellin $A_3$

The high photoactivity of 3-dehydrogibberellin $A_3$ (X) in the crystalline phase and the marked dependence of the pathway followed in this reaction on the character of the substituent R have been established.[24,25]



(X): a) R = H
b) R = $CH_3$

(XI)

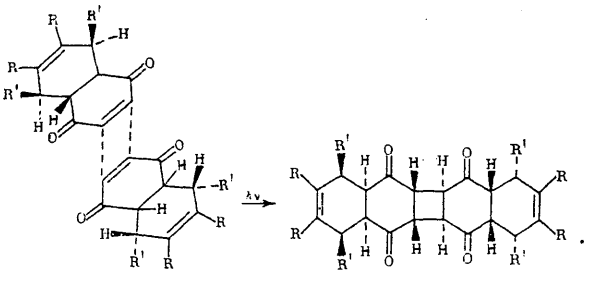
(XII) (XIII)

The enone acid (Xa) is decarboxylated as a result of the $n \rightarrow \pi^*$ excitation of the enone chromophore and is converted into the phenolic acid (XI) in a high yield,[26] while the corresponding methyl ester (Xb) dimerises with formation of compounds (XII) and (XIII) as a result of the intermolecular [2 + 2]-photocycloaddition of the C=C bond of the excited $\Delta^1$-enone ring to the terminal double bond of a neighbouring molecule. The molecular geometries of the ester (Xb)[27] and the acid (Xa)[28] are very similar. Fig. 3 illustrates the relative dispositions of the molecules of compound (Xb), involved in the solid-phase dimerisation reaction, which are packed "head to tail" into infinite chains around the $4_1$ axes (space group $P4_12_12_1$). The distance between the centres of the C(16)=C(17) and C(1′)=C(2′) double bonds in the neighbouring reacting molecules (3.71 Å) is favourable for topochemical reactions of this type.[2,29] The π orbitals of the double bonds of neighbouring molecules are located in approximately the same plane and are directed towards one another. The dihedral angle between the C(13)C(15)C(16)C(17) and C(1′)C(2′)C(3′)C(10′) planes is 19.7° and the torsional angle C(17)–[centre of C(16)–C(17) bond]–[centre of the C(1)–C(2) bond]–C(1) is 31.2°. Thus all the requirements for topochemical [2 + 2]-cycloaddition are met in the crystal of compound (Xb),[30] which makes it possible to predict the structure and stereochemistry of the main dimeric product (XIII) formed in 40% yield. The formation of the dimer (XII) as a side product is difficult to explain within the framework of the ideal topochemical model. Apparently this is a result of non-topochemical photodimerisation[29] caused by the imperfections of the initial crystal of compound (Xb).[2,30,31] It is believed[32,33] that the monomer molecules are able to rotate in the defective regions of this crystal in the intermediate excimeric state.

The different character of the solid-phase reactions on photoexcitation of compounds (Xa) and (Xb) has been explained by the different types of molecular packing in these crystals. In contrast to compound (Xa), in the crystal of compound (Xb)[28] the molecules are combined by hydrogen bonds into layers where the distance between the centres of the potentially active C(16)=C(17) and C(1)=C(2) double bonds is 4.5 Å and their π orbitals are oriented approximately at right angles, as a result of which only intramolecular photochemical reactions are possible.[27]

### 4. Derivatives of Naphthoquinone

Of the nine tetrahydronaphthoquinone systems whose structures have been investigated, only three [compounds (XVIa)–(XVIc)] are involved in topochemically controlled intermolecular reactions, forming the explosive dimers (XVIIa)–(XVIIc) via the [2 + 2]-photocycloaddition of the enedione double bonds of neighbouring molecules (the distances between the centres of their C=C double bonds are ≤4.04 Å).[34,35]

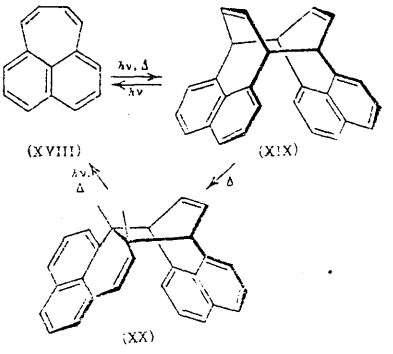


However, according to X-ray diffraction data, solid-phase intermolecular transfer of a hydrogen atom is also possible in compound (XVIb) (the $H_\beta$...O distances are 2.42 and 2.49 Å with the angles $\tau_O$ = 4° and 3° and $\Delta_O$ = 80.8° and

79.5°).§ Nevertheless, in the given instance the effect of the crystal packing, which favours a bimolecular reaction, predominates over the entropy factors, which usually promote a unimolecular reaction. This conclusion emphasises yet again how important it is to take into account the characteristics of the molecular packing in the crystal in formulating hypotheses about the course of photochemical reactions.[36]

### 5. 1,8-Naphthobicyclo[3.2.0]hepta-2,6-diene

Whereas prolonged irradiation of a solution of 1,8-naphthobicyclo[3.2.0]hepta-2,6-diene (XVIII) with ultraviolet light leads to the formation of a polymer and a small amount of naphthobicyclobutane, irradiation of the crystal with light in the visible region results in the appearance of the dimer (XIX):[37]




When the temperature is reduced to −195 °C, dimerisation ceases. On heating *in vacuo* to 150 °C, compound (XIX) isomerises quantitatively to the asymmetric dimer (XX), whose structure has been demonstrated by infrared spectroscopy and NMR. On irradiation with UV light at $\lambda = 313$ nm in solution, both dimers are readily converted into the initial monomer (XVIII).

In the crystal of compound (XVIII) at −196 °C the molecules are packed "head to tail" in pairs. On raising the temperature, the structure becomes disordered and the "head to head" arrangement appears within pairs of molecules, which leads to the formation of the dimer (XIX) for intermolecular distances permitting reaction in the solid phase. A decrease of temperature to −195 °C prevents the disordering and photodimerisation does not take place.

The molecule of compound (XIX) has a strained structure: the naphthalene fragments are not entirely non-planar, the valence angles at the peri-carbon atoms have been reduced to 113.2°, and the C–C bridging bonds have been extended on average to 1.626 Å. The strain energy of the molecule of compound (XIX), which was estimated by comparing the enthalpy of activation $\Delta H^{\neq}$ for the reaction (XIX) → (XX) with the enthalpy of dissociation of compound (XIX), is ~60 kJ mol$^{-1}$.[37]

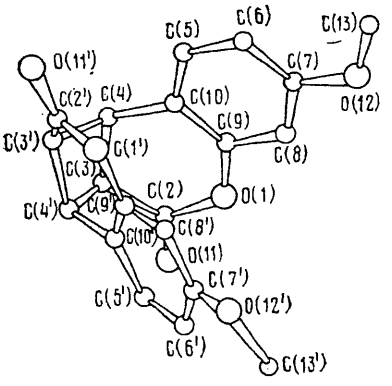



Figure 4. The structure of the 7-methoxycoumarin dimer (XXI); C(3)C(4)C(3′)C(4′) is the cyclobutane ring.[17]

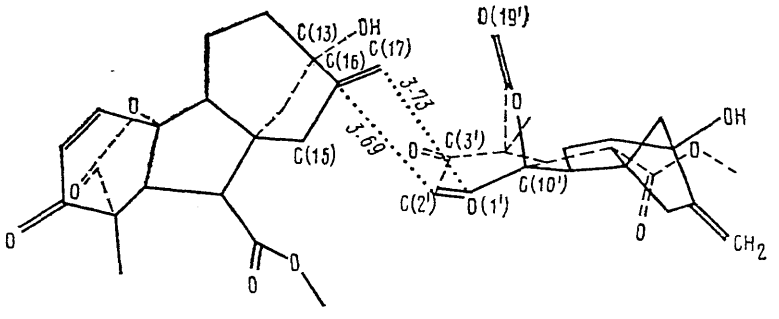



Figure 3. The relative disposition of the molecules linked by the $4_1$ axis in the crystal of compound (Xb).[28]

§ The crystal of compound (XVIb) is constructed from two symmetrically independent molecules; $\tau_0$ is the deviation of the atom $H_\beta$ from the plane of the carbonyl group and $\Delta_0$ is the $C(=O)H_\beta$ angle.

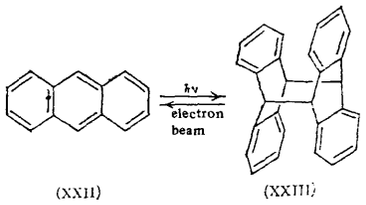
### 6. Coumarin Derivatives

Systematic crystallographic and photochemical studies have been made of the solid-phase dimerisation of ten coumarin derivatives.[17] The unsubstituted coumarin is photostable in the crystal, although it dimerises in solution.[38] On irradiation of the crystal with UV light, only 7- and 8-methoxycoumarins and 4-chlorocoumarin dimerise (the yields of the dimers are respectively 90, 50, and 40%). The dimer of 7-methoxycoumarin (XXI) has the *syn*-structure (head to tail arrangement, Fig. 4), but in the crystal of the monomer the orientation of the double bonds of neighbouring molecules, forming an angle of 115°, is topochemically unfavourable. It is suggested that the rotation of the molecules of compound (XXI) essential for their transition to the reactive state is possible at the screw dislocations of the crystal of compound (XXI). The photostability of the non-dimerising crystalline coumarin derivatives is due to the unfavourable relative disposition of the molecules in the crystals[17] and not to their special electronic or steric properties.

### 7. Anthracene Derivatives

The solid-phase dimerisation and dimer dissociation reactions as well as the processes preceding the dimerisation of anthracene and its derivatives have been investigated quite comprehensively. Studies of the crystal structures of anthracene derivatives before dimerisation showed that the final products do not always correspond to compounds whose formation is predicted by the topochemical reaction mechanism. Calculations for the possible local rearrangements in the molecular packing (the appearance of defects and dislocations), responsible for the formation of the final products, are therefore essential in many instances for the modelling of the dimerisation processes.

The anthracene (XXII) dimerises on irradiation and the crystal structure of the monoclinic modification of compound (XXII) does not satisfy the requirements for the occurrence of a topochemical reaction.[39]




(XXII) (XXIII)

It has been suggested that the relative orientation of the molecules of (XXII) convenient for dimerisation can arise at structural defects. Calculation of the energy of the displacement of one half of the crystal relative to the other along the (001), (010), (0$\bar{1}$0), (100), and (20$\bar{1}$) planes (atom–atom approximation) showed[40] that the displacement along the (010) plane should take place most readily, which corresponds to the direction of the dislocations most frequently observed in the anthracene crystal.[41] Analysis of the intermolecular distances changing as a result of the displacement showed that local molecular arrangements, favourable for dimerisation, can arise at the interface. However, Mirsky and Cohen[40] failed to take into account the changes in the disposition of the molecules (relaxation) near the defect, which led to unduly high displacement energies and to clearly unduly low interatomic distances.

The stabilities of point defects arising on the surface and in the bulk of the crystal of compound (XXII) on the removal of one molecule or on replacement of five molecules in the lattice by the more "freely" distributed four molecules have been estimated.[42] This calculation, carried out taking into account the relaxation of the molecular environment around the defect, showed that a defect can be thermodynamically stable and favourable for the subsequent rearrangement with participation of excited molecules.

The metastable triclinic phase of the anthracene (XXII) is formed when the monoclinic crystal is compressed in the direction at right angles to the basal plane. Its structure has been determined by electronic transmission microscopy and has been confirmed by the calculation of the molecular packing by the method of atom–atom potentials. It was found that the atoms interacting on dimerisation in the triclinic structure of compound (XXII) are closer together than in the monoclinic phase (the distance between them has been reduced from 4.5 to 4.2 Å). Calculation for the possible rearrangement of the two modifications on excitation of their molecules[43] failed to reveal changes sufficient to ensure the topotactic formation of the dimer. Consequently the occurrence of the reaction at structural defects is extremely probable.

A similar picture has been observed also for anthracene derivatives. Thus, when 1,5-dichloroanthracene is irradiated in solution with UV light, it is converted into a mixture of "head to head" (HH) and "head to tail" (HT) isomers in proportions of 40:60.[32] The solid-phase dimerisation of the monoclinic form leads to the formation of a dimer of the HH type (the reacting atoms of neighbouring molecules are at a distance of 4.05 Å).[30] The crystalline structure of the triclinic modification formed on dimerisation of a mixture of 80% of the HH isomer and 20% of the HT isomer has been determined by the method of atom–atom potentials.[30] A distance of 4.0 Å between the translationally linked molecules in this structure corresponds to the topochemical mechanism of the formation of the HH isomer. The study of the planar or linear defects showed that the symmetry of the given lattice makes it impossible to find a displacement which would lead to the formation of a dimer of the HT type. Presumably some of the molecules acquired an orientation favouring the formation of the HT dimer on rotation during the crystallisation process, i.e. a point defect appeared. Calculation of the energy of such defects, which is defined as the difference between the energies of the interaction with the environment of the "defect" molecule and the molecule in the ideal lattice has shown[44] that it amounts to ~4 kJ mole$^{-1}$ in the triclinic structure and ~100 kJ mol$^{-1}$ in the monoclinic structure. These differences explain the ease of formation of defects and the appearance of two dimeric products in the triclinic structure.

Dimerisation in the crystals of 1,8-dichloro-9-methylanthracene (XXIV)[45] and 1,8-dichloro-10-methylanthracene (XXV)[30] entails the formation of *cis*-products which are not due to a topochemical reaction. Energy calculation for compound (XXIV)[45] has shown that the appearance of planar defects "preparing" for the formation of the *trans*-dimers is possible. Modelling and electron microscope study of the dislocations in the crystal of compound (XXV)[46] made it possible to explain analogously the formation of dimeric products in this case also. Processes involving the formation of excimers and rearrangements occurring in the crystal lattice under these conditions have been examined in fair detail for anthracene and its derivatives both experimentally and with the aid of computational models. The results of studies devoted to these questions are discussed in the next Section.

### 8. Excimers in Crystals

Excimers were first detected in concentrated pyrene solutions, which exhibited unusual spectroscopic properties on irradiation compared with dilute solutions.[47] Later excimers were found also in pyrene crystals.[48] Experiment showed that excimers are formed throughout the bulk of the crystal and not only at structural defects. The molecular planes are almost fully overlapped to the maximum extent and approach one another. The formation of excimers is most probable when such overlap obtains already in the initial crystal structure.

Various computational models have been used to describe the geometry and spectroscopic characteristics of excimers (excimer emission).[49-51] The interactions of the pair of molecules in the excimer are usually assessed semi-empirically by quantum-chemical methods, while the interactions with the environment in the crystal are assessed in terms of the atom–atom approximation. Other parameters, characterising the dispersion interactions, which change as a result of the polarisation or excitation of the molecule, are sometimes specified (within the framework of the atom–atom approximation) for the excited molecule.

In the free pyrene excimer the molecular planes overlap fully and the distance between them becomes 3.2 Å. For such mutual approach of the molecules in the crystal, it is essential to displace them by approximately 0.7 Å, which involves the overcoming of an energy barrier of ~15–20 kJ mole$^{-1}$.[50] Analogous results have also been obtained in the calculation for the α-form of perylene.[51]

Many compounds, in the crystals of which excimers arise on irradiation, tend to undergo photodimerisation reactions. Since the formation of the excimer involves the mutual approach of two molecules and an increase of the degree of overlap of their planes, the excimer can be regarded as a dimerisation intermediate. This has been demonstrated in relation to a series of anthracene derivatives[51-53] which have three types of characteristic packing in the crystal: (1) "herring bone" packing without the overlap of the planes of the nearest molecules (type A) (both anthracene modifications); (2) stacked packing with a "head to head" arrangement—type B1 (9-cyano-, 9-chloro-, 9,10-dichloro-, and 9-carboxy-anthracene); (3) packing with a "head to tail" arrangement of molecules in pairs—type B2 (9-methyl- and 9-amino-anthracene). Emission of the monomer type only is observed in type A crystals,[52] while in crystals of types B1 and B2 the overlap of the molecular planes is significantly greater, excimers and dimers being formed in them; the frequencies change to the greatest extent in type B2 compounds on transition to the excited state.

The possible changes in the relative disposition of the molecules in crystals following the appearance of an excited molecule in the latter have been calculated by the method of atom–atom potentials[54] for two modifications of anthracene and its derivatives—9-cyanoanthracene (XXVI) and 9-methylanthracene (XXVII), which are characterised by different types of packing. Following the appearance of an excited molecule in the crystal of compound (XXII), the disposition of the molecules surrounding it hardly changes, which agrees with the absence of excimer emission. Dimers apparently are not formed in the bulk of the crystal, which does not rule out dimerisation on the surface and on defects.[54] In crystals of compound (XXVI) the excited molecule approaches one of the neighbouring molecules in the stack and the surrounding molecules are "drawn" towards this pair. Since in the given instance the dimerisation products contain only the *trans*-dimer (and not the *cis*-dimer, which corresponds to a topochemical mechanism), presumably the excitation energy of the *cis*-excimers is transferred to structural defects, where the *trans*-dimer is formed. In crystals of compound (XXVII) (type B2), the excited molecules are appreciably displaced towards one of the molecules in its environment, while the positions of the remaining surrounding molecules change little. The absence of steric hindrance and the antiparallel directions of the molecular dipole moments, as in the second modification of 9-chloroanthracene (likewise type B2), permit dimerisation throughout the bulk of the crystal.[54]

The most striking examples of the intermediate formation of excimers are provided by the decomposition and redimerisation in the crystal of dianthracene (XXIII).[44] If a single crystal of compound (XXIII) is subjected to high-energy irradiation, some of the dimer molecules are cleaved into pairs of monomers. Exposure to low-energy irradiation leads to excimer emission and the redimerisation of the monomer molecules. The quantum yields of both processes depend on temperature. Thus, together with dimerisation, the excimer emission serves as a pathway leading to the deactivation of the excimer.

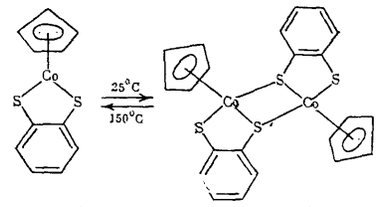
Calculations carried out in terms of the atom–atom approximation, which models the processes described above, have shown[55] that the formation of dianthracene crystals incorporating pairs of anthracene molecules is energetically more favourable than the formation of crystals of dianthracene alone as a result of the increase of the intensity of the non-valence interactions in pairs of molecules compared with the dimer.[55] In our view, a special physical significance should not be attributed to the energy differences observed, but it is clear that the dissociation of the dimer does not induce a significant steric hindrance in the lattice. According to the calculation, the disposition of a pair of molecules of compound (XXII) in the dianthracene matrix is such that their planes do not overlap fully. Hence one can understand the necessity for the expenditure of energy in order to overcome the barrier to the formation of the excimer or to redimerisation.[55]

Excimers are also formed in crystals made up of planar aromatic molecules. Thus excimer emission and photodimerisation are characteristic of two crystalline forms of 2,4-dichloro-3-methylstilbene.[56] In one of the modifications with a stacked molecular arrangement *cis*-excimers and dimers with *m* symmetry are formed. In the other modification, with molecules which have approached one another in pairs, *trans*-excimers and centrosymmetric dimers arise. Thus, in the given instance the structure of the dimer is determined by the same characteristics of the crystal packing as the structure of the excimer.

The formation of excimers in a crystal made up of non-rigid molecules (analogous to those mentioned above) is a more complex process than for rigid aromatic molecules. According to calculations, the photodimerisation of 1-(2,6-dichlorophenyl)-4-phenylbutadiene is accompanied not only by the mutual approach of the molecules but also by a change in their conformation.[57,58] It has been shown that the excimer can be obtained in two ways presupposing the approach to one of two neighbouring molecules in the stack, requiring approximately identical energy expenditures. At any rate, it follows from the results of the calculation taking into account the molecular relaxation that the excimer has an asymmetric environment. The real pathway followed in the dimerisation reaction can be deduced only by determining the structure of the monomer and the products formed by X-ray diffraction. Calculation for 1-(2,6-dichlorophenyl)-4-phenylbutadiene does not rule out the appearance in the crystal not only of excited dimers but also of trimers.

### 9. Cyclopentadienyl(*o*-phenylenedithio)cobalt

The dimerisation of cyclopentadienyl(*o*-phenylenedithio)-cobalt is an example of a rarely encountered reversible solid-phase process (XXVIII).[48]




(XXVIII) (XXIX)

In the crystal of compound (XXVIII) the molecules are arranged "head to tail" and, although the Co...S intermolecular distances [4.702 and 4.325(1), Å] are fairly large, the relative disposition of the "heavy" atoms (Co and S) resembles that observed in the crystal of the dimer (XXIX). In the course of the solid-phase transition the coordination of the cobalt atom changes from the "two-legged" type in compound (XXVIII) to the "three-legged" piano stool type in compound (XXIX). The slope of the plane of the $\eta^5$-$C_5H_5$ ring relative to the S–Co–S plane changes by 45° on passing from compound (XXIII) to compound (XXIX). Whereas the metal-containing ring in compound (XXVIII) is almost planar (the maximum deviation is 0.02 Å), in compound (XXIX) the ring is bent along the S...S line by 20.9°.

The solid-phase dimerisation of compound (XXVIII) takes place as a result of the mutual approach of its molecules (predominantly in the direction of the *b* axis) and increases the density of the crystal by 6%. The orientation of the axes in the crystals of compounds (XXVIII) and (XXIX) (which belong to the same space group $P2_1/c$) is not the same and the reaction is not topotactic. At 25 °C the dimerisation is fairly slow owing to the relatively high "rigidity" of the potential energy surface of the crystal. Furthermore, the development of the reaction requires defects—nucleation centres. The rate of the reverse reaction (XXIX) → (XXVIII), which depends on the particle size, is low at 150 °C but rapidly increases at higher temperatures. The small enthalpy of monomerisation ($\Delta H$ = 18.9 kJ mol$^{-1}$ at 150–160 °C) found from data obtained by differential scanning calorimetry is consistent with data indicating the occurrence of conformational polymorphism and is insufficient for the occurrence of the reversible solid-phase reaction despite the considerable displacements of the atoms.[48]

The examples examined show that the combination of experiment (X-ray diffraction and spectroscopic methods) and calculation makes it possible to investigate various stages in the formation of dimers in the crystal. It may be that subsequently this approach will be applied also to the consideration of more complex solid-state reactions.

## III. REDIMERISATION

The redimerisation process in the crystal has been most thoroughly investigated for anthracene derivatives (see also above). It has been shown that the *trans*-dimer (XXX) of 9-cyanoanthracene (XXXI), formed by the solid-phase dimerisation on irradiation with UV light,[59] is capable of being reconverted into the monomeric form in the crystal on thermal or photochemical initiation,[60] which imparts practical importance to this reversible process, for example, for the reversible absorption of solar energy.[61] The study of crystals by differential scanning calorimetry has revealed the presence of two exothermic peaks, the second of which corresponds to the complete conversion into the monomeric form and the first (at 152 °C) corresponds to a homogeneous topotactic single crystal → single crystal phase transition of the colourless triclinic crystal of compound (XXX) into the yellow, also triclinic, crystal of compound (XXX'). The driving force of this polymorphic transformation is partial conversion into the monomeric form [the admixture of the monomer (XXXI) in the crystal of compound (XXX') amounts to 8%].[60]

Pyrimidines and their *N*-methyl derivatives dimerise on UV irradiation in the solid phase via their double bonds in the 5- and 6-positions. Depending on the disposition of the dihydropyrimidine rings relative to the cyclobutane ring formed on dimerisation, four stereoisomeric forms of the dimer are possible: *cis, syn-*, *cis, anti-*, *trans, syn-*, and *trans, anti-*.[62] The structures of ten dimers of all four types have been determined,[63] including the *cis, syn*-form encountered in DNA[64] and two dimers (of the *trans, anti*-type) of thymine and 1-methylthymine.[65]

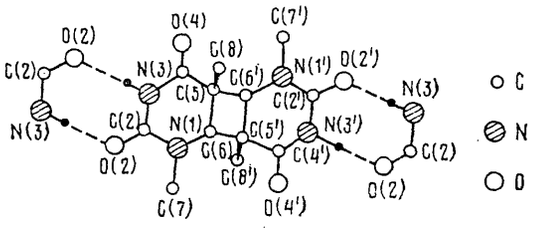



Figure 5. A fragment of the crystal structure of compound (XXXII); the N–H...O hydrogen bonds linking the molecules of compound (XXXII) into infinite chains in the [110] direction are shown dashed.[66]

The thymine dimers are cleaved in solution on irradiation with UV light[66] or X-rays.[67] The solid-phase conversion into the monomeric form on exposure to $^{60}$Co γ-rays of the crystals of all four stereoisomers of the *NN*-dimethylthymine dimer[68] or in the course of X-ray measurements on three dimers of the *cis, syn*-type[69] is also possible. X-Ray diffraction study of the 1,1'-trimethylenethymine dimer revealed the presence of ~10% of monomeric molecules incorporated in the dimer crystal.[70] The possibility of the conversion into the monomeric form has been reported by the investigators of the structure of the 1,3-dimethylthymine dimer (a sharp increase in the length of one of the interpyrimidine bonds to 1.66 Å), but the monomeric molecules could not be located.[71] A third example is provided by the sodium salt of the thymine dimer, in the crystal of which monomer molecules were found.[72]

We shall consider the structure of the *trans, anti*-dimer of 1-methylthymine (XXXII).[66] The molecules of compound (XXXII), combined in the crystal into infinite chains along the [110] direction by N(3)–H...O(2) bonds (Fig.5), show no signs of the steric strain observed in the dimers of the *cis, syn*-type, which also associate in the crystal on irradiation with X-rays [the steric strain is shown by the shortened intramolecular distances between the methyl groups at the C(5) and C(5') atoms[70–72]]. Nevertheless the crystal of compound (XXXII) contains ~4% of the monomer molecules

formed as a result of the solid-phase dissociation on irradiation with X-rays in the course of the structural study. This result confirms data[64] indicating the possibility of the solid-phase dissociation on irradiation of unstrained stereoisomeric dimethylthymine dimers with X-rays.

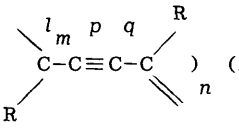
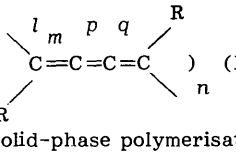
## IV. POLYMERISATION

The greatest advances have been made in the field of topochemical solid-phase non-diffusional polymerisation of diacetylenes, which proceeds via 1,4-addition. Reports about these processes appeared a long time ago (the crystals of diacetylenedicarboxylic acid darken on illumination and irradiation with X-rays[73]), while the most important results were obtained approximately 15 years ago by Wegner[74-76] and Baughman.[77] The second field involved the study of solid-phase topochemical polymerisation reactions of diolefins. The investigations began after the report of the ability of the α-modification of 2,5-distyrylpyrazine to polymerise as a result of the photoinduced [2 + 2]-polycycloaddition[78,79] although data concerning the possibility of the occurrence of the process had appeared considerably earlier.[80]

A number of other systems which polymerise in the crystal subject to more or less vigorous topochemical control are also known.[80] Compared with the first two systems (diacetylenes and diolefins), they are less important. Among them, mention should be made in the first place of the cyclic oligomers of formaldehyde, which are capable of polymerisation with the opening of the ring. Although a distinct topotactic interrelation is observed between the starting materials and final product in this process, the latter is not topochemical. This reaction has been considered in detail in a review.[80]

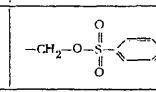
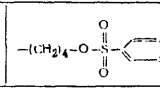
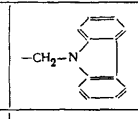
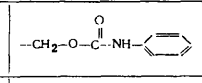
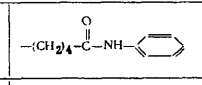
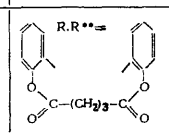
### 1. 1,4-Addition of Diacetylenes

The solid-phase polymerisation of diacetylenes (DA), which makes it possible to obtain large single crystals of polydiacetylenes (PDA), is a fairly thoroughly investigated reaction (see the relevant reviews[80-83]). Nevertheless studies in this field still remain timely, mainly in connection with the vigorous development of research in the field of conducting organic systems.

The solid-phase polymerisation of the diacetylene R–C≡C–C≡C–R, which is initiated either by heating to temperatures below the melting point, or by irradiation with γ-rays or UV light, or by other influences, constitutes poly-1,4-addition. The products of this reaction consist of quasi-one-dimensional macromolecules with a conjugated skeleton fully in the *trans*-configuration.[74-77] Two limiting structures of PDA are possible: the ene-yne (ethylene–acetylene structure  (A) and the butatriene (cumulene) structure  (B); in the real PDA, obtained by the solid-phase polymerisation of DA (Table 2), both structures have been detected, although structure (A) predominates.[78,84-88]

Numerous studies have been devoted to the physicochemical properties of PDA (see, for example, Yee and Chance[82]). The thermal stability of PDA can be both low [compound (XXXIIIp) decomposes at temperatures not

Table 2. Principal structural parameters of PDA obtained by the solid-phase polymerisation of R–C≡C–C≡C–R.

| Compound | R | Structure | Bond length, Å | | | | Space group, direction of chain | Refs. |
|---|---|---|---|---|---|---|---|---|
| | | | *l* | *m* | *p* | *q* | | |
| (XXXIIIp) |  | (A) | 1.356 (4) | 1.428 (4) | 1.191 (4) | 1.428 (4) | $P2_1/c$, $Z = 2/n$; chain along $b = 4.910$ (3) Å | [83] |
| (XXXIVp) |  | (A) | * | * | * | * | $P\bar{1}$, $Z = 2/n$; chain along $c = 4.91$ (1) Å | [85] |
| (XXXVp) |  | (A) | 1.33 (2) | 1.44 (2) | 1.21 (2) | 1.44 (2) | $P2_1/c$, $Z = 2/n$; chain along $b = 4.907$ (4) Å | [86] |
| (XXXVIp) |  | (A) | 1.36 | 1.41 | 1.21 | 1.42 | $P\bar{1}$, $Z = 1/n$; chain along $a = 4.89$ (1) Å | [87] |
| (XXXVIIp) |  | (B) | * | * | * | * | * | [86] |
| (XXXVIIp) |  | (B) | 1.42 (3) | 1.38 (2) | 1.29 (2) | 1.38 (2) | $C2/c$, $Z = 8/n$; chain along $c = 9.69$ Å *** | [88] |

*Literature data not available.

**The monomer unit has a cyclic structure.

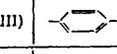
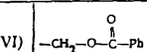
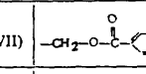
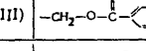
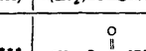
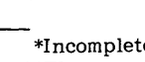
***The repeat period of the polymer chain is greater by a factor of approximately two than for (XXXIIIp)–(XXXVIp) in connection with the different (*trans*) disposition of the cyclic substituents relative to the PDA chain.

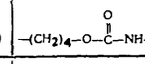
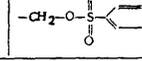
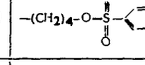
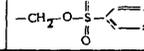
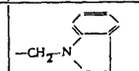
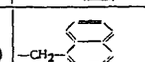
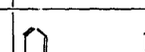
exceeding 70 °C[89]] and very high [the weight loss of compound (XXXVIIp) is 2.5% at 300 °C,[90] while compound (XXXVp) is stable up to 300 °C and at 400 °C its weight loss does not exceed 6.5%]. Whereas the thermal stability of compound (XXXVIIIp) has been accounted for by the stabilising effect of bisphenylglutaric chains forming a ring on the polymer chain, the thermal stability of compound (XXXVp) is associated with the stability of the carbazolyl substituent [furthermore, a high mechanical strength is characteristic of compound (XXXVp)[82]].

The electrophysical properties of PDA are of special interest. Although these polymers remain insulators under the usual conditions[91–95] [for example the average conductivity of compound (XXXIIIp) is $\sigma = 10^{-15}\ \Omega^{-1}\ cm^{-1}$ [82]], the PDA crystals exhibit anisotropic conductivity.[81] At the same time, by doping the DA crystals with iodine and by subsequent solid-phase polymerisation under the influence of γ-irradiation, it is possible to obtain PDA with metallic lustre and $\sigma = 10^{-4}\ \Omega^{-1}\ cm^{-1}$.[93] The photoconductivity of PDA has been investigated.[82,94] The lowest optical transition energy (1.89 eV) is that of the crystals of compound (XXXIIIp).[82] The appreciable hypsochromic shift of the photoconductivity spectra of PDA relative to the optical absorption spectra is consistent with the exciton mechanism of the optical transitions with the minimum energy in PDA.[82]

The study of the structure of PDA is of special interest for two reasons. Firstly, the polymerisation of DA is possible only under lattice control and is not observed in the melt, in the gas phase, or in solution.[81] Secondly, data for the structure of PDA are important in connection with the similarity of these polymers to polyacetylenes—an important class of organic metals, the elucidation of the structure of which (particularly in doped systems) is fairly difficult.[95]

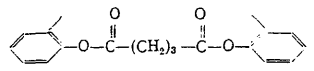
Table 3. The principal data on the reactivities in solid- phase polymerisation and molecular packing in crystals of the structurally investigated diacetylenes of the type R–C≡C–C≡C–R (for the significance of the parameters $S_1$, $\gamma_1$, and $d_1$, see Fig. 6).

| Compound | R | Reactivity | Parameters of the relative disposition of the stacked DA molecules | | | Refs. |
|---|---|---|---|---|---|---|
| | | | $S_1$, Å | $\gamma_1$, deg | $d_1$, Å | |
| (XXXIX) | $-CH_2OH$ | +* | 3.94**<br>3.54 | 41.4<br>53.4 | 4.77<br>5.34 | [96] |
| (XL)*** | $R^1 = -CH_2$; $R^2 = -CH_2OH$ | +* | 3.71 | 49.6 | 4.87 | [97] |
| (XLI) | $-(CH_2)_2-OH$ | + | 3.65 | — | — | [98] |
| (XLII) | $-Ph$ | — | 4.69 | 50.9 | 6.04 | [99] |
| (XLIII) |  | — | — | — | — | [100] |
| (XLIV) | $-CH_2-O-Ph$*** | — | — | 73 | 7.47 | [101] |
| (XLV) | $-C(OH)Ph_2$ | — | — | — | — | [102] |
| (XLVI) |  | — | 4.02<br>6.11 | 58.8<br>40 | 4.35<br>8.48 | [103] |
| (XLVII) |  | + | — | — | — | [104] |
| (XLVIII) |  | — | — | — | — | [105] |
| (XLIX) |  | — | — | — | — | [106] |
| (L)**** |  | + | — | — | — | [107] |

| Compound | R | Reactivity | Parameters of the relative disposition of the stacked DA molecules | | | Refs. |
|---|---|---|---|---|---|---|
| | | | $S_1$, Å | $\gamma_1$, deg | $d_1$, Å | |
| (LI) |  | + | — | — | — | [106] |
| (LII) |  | + | — | 44**<br>46 | 5.11 | [108] |
| (LIII) |  | + | — | 47.9 | 5.19 | [85] |
| (LIV) |  | — | — | 67.0 | 5.030<br>4.962***** | [109] |
| (LV) |  | — | — | 90 | 5.977***** | [110] |
| (LVI) |  | +****** | — | 60 | 4.55 | [111] |
| (LVII) |  | — | — | 61.5 | 4.35 | [111] |
| (LVIII)**** |  | +*<br>— | —<br>— | 46<br>90 | 4.93<br>5.42 | [112] |

*Incomplete conversion.
**There are two types of intermolecular contacts in the crystal with participation of diacetylene fragments.
***Asymmetric DA of the type $R^1-C\equiv C-C\equiv C-R^2$.
****Two polymorphic modifications have been investigated.
*****Intermolecular distance between atoms potentially capable of reacting.
******Phase transition on polymerisation.
*******Cyclic DA.

Apart from the linear DA (XXXIX)–(LVII), the solid-phase polymerisation of the cyclic DA (LVIII) (Table 3) with formation of a fully stereoregular polymer (XXXVIIIp), whose skeleton is threaded by ring-forming *oo*-bisphenylglutarate groups, has also been investigated:[90,112,113]



The capacity for solid-phase polymerisation of the even more complex macrocyclic DA $[-(CH_2)_2-C\equiv C-C\equiv C-(CH_2)_2-]_4$ (LIX) has been observed. As a result of the 1,4-addition via all four diacetylenic groups, this compound is converted into an ordered polymer with a "cylindrical" structure.[114]

The conditions governing the formation of large defect-free crystals of PDA by the solid-phase polymerisation of DA have been analysed.[115]

1. The free energy barrier to cooperative displacements of the DA molecules, necessary for their polymerisation, increases (i.e. the capacity for polymerisation diminishes) with increase of the displacement of the interacting molecules necessary for the reaction.

2. The polymeric molecules must be capable of forming solid solutions in the crystal of the polymerising matrix at any degree of conversion (single-phase or homogeneous polymerisation).

3. The symmetry of the crystal environment of the monomer molecules must correspond to the symmetry of the environment of the monomeric unit of the polymer molecule.

By varying the reaction conditions, it is in many instances possible to promote single-phase polymerisation, in particular, by imposing an external force field it is possible to alter the symmetry of the monomer crystal.[115] However, only polycrystalline PDA are formed in the polymerisation of certain DA. This happens in those cases where the nucleation of the new phase (the solid-phase polymerisation can be regarded as a special type of phase transition) occurs on defects, surfaces, or impurities in the monomer crystal.[81] In principle, such processes can lead to the formation of large PDA crystals (when the polymerisation and crystallisation take place simultaneously). On the other hand, the topotaxy in the initial and final phases does not necessarily indicate the topochemical character of the solid-phase transition.[81]

We shall consider the mechanism of chain propagation in the monomer crystal matrix. The following scheme has been proposed for this process: thermal (or radiation-induced) excitation of the conjugated triple bonds with transition to intermediates of the dicarbene type, combination of the dicarbenes with formation of double bonds, and growth of the macromolecule as a result of further addition of excited molecules to the carbene-like end of the chain.[81] The formation of biradical dimeric, trimeric, and tetrameric, etc. intermediate compounds has been detected by EPR[116–119] and optical spectroscopic[120,121] methods in the study of the solid-phase transition (LIII) → (XXXIVp). The most probable chain length of the PDA macromolecules in the polymerised crystal of compound (XXXIVp) has been estimated by gel-permeation chromatography. It amounts to 1600 monomeric units when the polymerisation is carried out at 7 °C and to 400 units at −263 °C. The difference is attributed to the different mechanisms of the polymer chain propagation.[85]

The condition governing the solid-phase reactivity (the Schmidt condition[2,10,122]), which has been extended in a general form to polymerisation by Kargin and Kabanov,[123] has been formulated by Wegner (see, for example, Shklover et al.[80]) and Baughman (see, for example, Ref.77) on the basis of the analysis of the crystal structures of DA active and inactive with respect to solid-phase polymerisation. This condition reduces to the following limiting values of the parameters $S_1$ and $\gamma_1$ of the molecular packing of DA, generating ladder (stacked) motifs in the crystals: $3.4 \leq S_1 \leq 4.0$ Å; $\gamma_1 \cong 45°$ (Fig.6). In the polymer, $d_2 = 4.9(1)$ Å and $\gamma_2 = 13.5°$.[77,80]

The rates of the solid-phase polymerisation of the chemically very similar compounds (XLVII) and (XLVIII) differ sharply: compound (XLIV) reacts much faster.[104,105] In the crystal of compound (XLIV), the values of $S_1$ (3.36 Å) and $\gamma_1$ (42.4°) satisfy the Wegner–Baughman conditions. In the crystal of compound (XLVIII) two types of relative dispositions of the molecules have been distinguished: the δ-type ($S_1 = 3.817$ Å and $\gamma_1 = 67.54°$) and the δ′-type ($S_1 = 4.643$ Å and $\gamma_1 = 63.44°$). In the former case the solid-phase interaction is significantly hindered, while in the latter case it is impossible.[104,105]

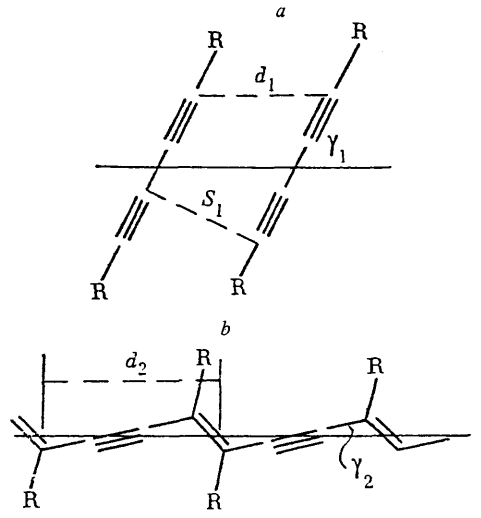



Figure 6. Schematic illustration of the packing of DA crystals with a ladder disposition of the molecules (*a*) and the structure (fragment) of the PDA molecules formed on polymerisation of DA via the "scissors" mechanism (*b*).[77,80]

It is of interest that an appreciable infringement of the "scissors" mechanism of the polymerisation of DA has been observed for the solid-phase reaction (LIII) → (XXXIVp) (Fig.6): the centre of gravity of the DA fragment shifts on polymerisation by 0.97 Å.[85] The possibility of such a shift without the breakdown of the crystal lattice structure can be explained by the fact that the toluene-β-sulphonate groups occupy pseudocentrosymmetric positions in the crystal, i.e. they retain their positions on transition to the centrosymmetric crystal of compound (XXXIVp).

The solid-phase polymerisation of the monomer (L), the only reactive DA in the crystal of which the DA "rods" are not parallel but are arranged at an angle of 72°, may constitute an exception to the "scissors" mechanism. The solid-phase transition of the monomer (L) on treatment with dioxan vapour to a very rapidly polymerising modification containing dioxan of crystallisation is also unusual.[106]

## 2. Polymerisation of Olefins

The topochemically controlled solid-phase polymerisation has found many applications in the past years. The synthesis from achiral precursors of chiral polymers, which are new materials for optical devices,[127] has been reported.[9,124-126] Goldanski[128] discovered reactions at extremely low temperatures whose rate is independent of temperature. However, the mechanism of the topochemical polymerisation has not so far been elucidated. In particular, it is not clear whether the crystal structure of the monomer controls all or only some of the three main processes: initiation of polymerisation, propagation of the polymer chain, and crystallisation. The role of the microstructure, in particular of the imperfections of the monomer crystal, has been inadequately investigated. A review[129] has been devoted to the discussion of these questions in terms of the results of X-ray diffraction and electron microscopy experiments. The crystallographic data for monomer–polymer pairs and the crystal structures of 11 diolefinic monomers are considered in this review.

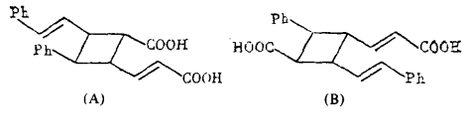
The main conclusion is that the principle of topochemical control formulated by Schmidt[2] plays a decisive role in the four-centre polymerisation of diolefins. In contrast to diacetylenes, many diolefins are available for X-ray diffraction study in both monomeric and polymeric states,[77,130] which makes it possible to determine the topotactic relation between the initial phase and the polymerisation product.[5] Three types of systems have been discovered: (a) all three crystallographic axes of the polymer and monomer crystals coincide (the difference between the volumes of the unit cells is small); (b) the directions of only one axis, along the polymer chain, coincide; (c) the directions of all three axes do not coincide. Although the changes in the unit cell parameters of all the systems investigated are fairly significant on polymerisation [up to 13% for 2,5-distyrylpyrazine (LIX)], the change in the unit cell is small [less than 2% for compound (LIX)].[129] The space group of the monomer crystal is as a rule retained on polymerisation. The solid-phase polymerisation of diolefins always occurs with topochemical control but the strains induced by this process in the lattice of the initial compound lead in all the cases investigated to the fragmentation of the monomer single crystal and the formation of a polycrystalline product.[129]

The role of the rigid lattice in solid-phase polymerisation has been confirmed by data for the reaction of diethyl *p*-phenylenebisacrylate (LX), whose polymerising centrosymmetric modification has a melting point of 96 °C. After the irradiation of crystals of compound (LX) at temperatures close to the melting point, an amorphous oligomer is formed; if the process is carried out at 0 °C, it is possible to obtain a crystalline polymer.[131] Thus, even if the initial reaction stages occur in the crystal lattice of the monomer, the topochemical control over the subsequent reaction stages is lost when the thermal energy evolved is comparable to the crystal lattice energy.[129]

Amorphous oligomers appear in the solid-phase reactions of diolefins in those cases where the translationally linked molecules react topochemically with formation of cyclobutane rings having the *m* symmetry. However, the primary products, the V-shaped dimers, disrupt the initial crystal lattice to such an extent that the distances between the reacting double bonds become too great. In other words, the monomer lattice breaks down at the dimerisation stage and the subsequent formation of the amorphous oligomer is not subject to rules of any kind.[130,131] It has been found that the solid-phase oligomerisation of dimethyl 4(2-carboxyvinyl)-α-cyanocinnamate (LXI) takes place in this way.[132]

The molecules in the crystal of compound (LXI) are packed in stacks along the $c = 3.956(1)$ Å axis, in contrast to the crystals of photo-diolefins, where the lattice period along the stacks, formed by molecules displaced by one half of the molecular length, is ~7 Å.[133] Thus the translation of *c* in the crystal of compound (LXI) corresponds to the shortest distance between the reactive double bonds, which is close to that found in photopolymerising crystals (on average 3.94 Å)[132] and differs from the crystals in photostable crystals (for example 4.187 and 4.369 Å[15]). The next distance in terms of magnitude between the double bonds of the molecules of different stacks in the crystal of compound (LXI) exceeds 5 Å. The molecules of compound (LXI) apparently interact within the stacks with formation of cyclobutane derivatives having the mirror symmetry. Such a reaction infringes the ordered arrangement of the molecules in the rest of the monomer crystal and for this reason only an amorphous oligomer is produced.[132]

Kashino and Haisa[134] investigated the geometrical conditions governing the solid-phase reactivity in crystals of two noncentrosymmetric diolefins: 5-phenylpenta-2,5-dienoic acid (LXII) and 1,5-diphenylpenta-2,4-dien-1-one (LXIII), of which the first exhibits solid-phase reactivity. The molecules in the crystal of compound (LXII) are combined via O–H...O hydrogen bonds into dimers whose axes are approximately parallel to the [0$\bar{1}$4] direction. The dimers are in their turn combined into broad strips. The distances between the approximately parallel double bonds (4.07 and 4.42 Å) are favourable for the formation of a type (A) dimer on irradiation of crystals of compound (LXII).[135]




(A) (B)

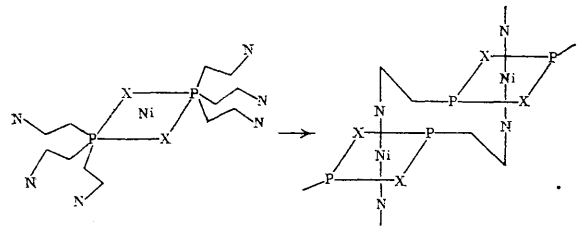
The angle between the interacting double bonds, which is 28°, can be reduced as a result of thermal movement. In the crystal of compound (LXII) it is also possible to distinguish pairs of molecules in which the mutual orientation of the double bonds promotes the preferential formation of the dimers (B).[135] However, in this case the distance between the double bonds (4.56 and 4.62 Å) is somewhat greater than in photopolymerising crystals.[2] On the other hand, it is possible to distinguish pairs of molecules in which the distance between the double bonds does in fact allow interaction (3.60 and 4.46 Å), but their inclination at an angle of 87° rules out the possibility of reaction in this direction according to the authors.[135]

In the crystal of compound (LXIII) the double bonds in neighbouring overlapping molecules have not approached one another and are not parallel, in contrast to, for example, the photopolymerising crystals of *trans*-cinnamic acid[136] and diphenyl *p*-phenylenediacrylate.[134] The gap of 5.31 Å between the nearest parallel C(4)...C(5) bonds greatly exceeds 4 Å, i.e. the distance necessary for dimerisation.[2]

An attempt has been made to interpret the solid-phase polymerisation process in relation to model crystals of ethylene[137-140] and formaldehyde.[141] Using quantum-chemical methods and the method of atom–atom potentials, calculations have been made of individual sections of the potential energy surface which suggested that the nuclei of the polymer chain are located in non-equilibrium positions between the crystal lattice sites; chain propagation takes place as a result of the migration of the chain nucleus in the crystal, which does not require an energy expenditure. Unfortunately, the alternative dislocation mechanism of the process was not considered in the above studies.

### 3. Thermal Polymerisation of the $NiHal_2L_2$ Complexes

The red square monomeric complexes $NiHal_2L_2$ [Hal = Cl or Br; L = $P(CH_2CH_2CN)_3$] are converted on standing into the blue polymers $(NiHal_2L_2)_x$ with the octahedral coordination of the Ni atom.[142]



Only one of the three cyanoethyl groups of each ligand L participates in the polymerisation. X-Ray diffraction study of the monomer, the polymer (its crystals were grown in solution), and also partly polymerised monomer crystals established that the volume of the unit cell of the complex $NiBr_2L_2$ changes only slightly on polymerisation (2459 and 2467 Å$^3$ for the monomer and polymer respectively) and the length of the lattice period *c* hardly changes at all (8.49 and 8.50 Å).[142] The reaction is heterogeneous and the monomer and polymer are not isomorphous. The topotactic relation between the crystal lattices of the monomer and polymer and the crystallographic direction of the propagation of the polymer chain, namely [101], have been determined. The identity of the polymers obtained by polymerisation in the crystal and in solution has been demonstrated.[142,143]

The monomer $NiCl_2L_2$ exhibits the lowest reactivity. Thermal depolymerisation before fusion is characteristic of the polymer formed. The volume of the monomer unit cell is smaller than that of the polymer (2386 and 2402 Å$^3$ respectively). The changes in the lattice identity period are somewhat greater than for the bromo-complex. Furthermore, not one direction of the propagation of the polymer chain, as in $NiBr_2L_2$, but two such directions, namely [101] and [10$\bar{1}$] have been observed for $NiCl_2L_2$ crystals, which leads to a different orientation of the polymer macromolecules in the crystal produced.[142]

The directions of growth of the macromolecules in the doped $NiBr_{1.84}I_{0.16}L_2$ {the [201] direction} and initial $NiBrL_2$ crystals are different, the difference being attributed,[142] in particular, to the character of the disposition of the dopant atoms and of the defects introduced by them approximately in planes perpendicular to the [201] direction.

The complexes $Ni(SCN)_2L_2$, $Ni(CN)_2L_2$, and $NiI_2L_2$ do not polymerise either in the solid phase or in solution. On the other hand, the $Ni(NCS)_2L_2$ crystals exhibit other interesting properties: conformational polymorphism and capacity for martensite-like phase transitions.[142]

## V. ASYMMETRIC SYNTHESIS

Topochemically controlled reactions lead to new possibilities for asymmetric synthesis, frequently with a quantitative yield and in systems "convenient for control".[9,125,144] Furthermore, optically active compounds can be sometimes obtained as a result of the crystallisation of solutions of achiral starting materials and subsequent solid-phase reactions without any external asymmetric influence.[124,126] Studies on these lines, justly referred to as "absolute asymmetric synthesis", can bring us nearer to the solution of the more general problem of the appearance and spread of optically active compounds in biological systems.[124]

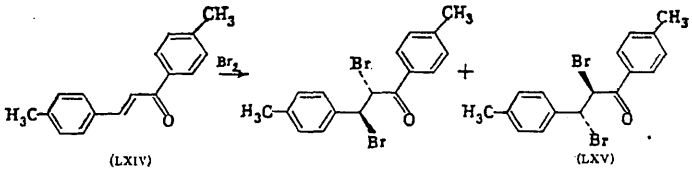
Asymmetric synthesis in the crystal has two aspects: the formation of chiral crystals and topochemically controlled solid-phase reactions with formation of chiral products. The very crystallisation process can be regarded as the simplest form of reaction, because the molecules in solution or in the melt usually assume an infinite number of conformations, while in crystallisation they have one or (more rarely) two conformations. Thus asymmetric induction is completed already in the crystallisation stage in the chiral structure; it only remains to transfer this chirality to the configurationally more stable form via a solid-phase reaction.[9]

Chiral crystal structures with definite intermolecular and intramolecular characteristics are essential for the systematic study of solid-phase asymmetric synthesis. This problem, which is part of the more general problem of crystal structure "engineering", so far has not had a general solution and studies on these lines are frequently heuristic.

A number of simple qualitative procedures for the synthesis of optically active products as a result of solid-phase reactions are known. For example, carboxylic acids and their primary and secondary amides tend to form centrosymmetric hydrogen-bonded dimers, i.e. they crystallise in centrosymmetric achiral space groups.[146,147] On the other hand, if the molecule contains a second functional group forming hydrogen bonds (−OH, >NH, S=O, etc), then, instead of centrosymmetric dimers, helical chains arise in the crystal, which increases the probability of the formation of crystals with a chiral structure.[148,149] Molecules with an intrinsic $C_2$ symmetry[150] and especially $C_3$ symmetry[9] tend to crystallise in chiral space groups. Clathrates, for example, those of urea and tri-*o*-thymotide, which form chiral crystals with incorporated achiral "guest" molecules, can be conveniently used to construct chiral crystal matrices.[151] The introduction of stable chiral groups into the molecule is believed nowadays to be the most reliable method for the synthesis of an achiral structure.[8]

We shall consider initially achiral or rapidly racemising molecules, which crystallise to give chiral crystals. If the inversion of the configuration is faster than crystallisation, there is a possibility of the formation of unequal amounts of enantiomorphic crystals with excess of one of the enantiomers. It is sometimes possible to obtain the entire substance in the form of a single enantiomorphic homochiral cyrstal.[152,156] The second case is one where the chirality of the crystal is determined by the molecular chirality. Asymmetric synthesis in such systems can be carried out in polycrystalline specimens, since asymmetric induction depends not only on the chirality of the molecules but also on the chirality of their environment in the crystal.

The first experimental confirmation of the possibility of the solid-phase asymmetric synthesis was provided by the interaction of the chiral 4,4′-dimethylchalcone single crystal with gaseous (or liquid) bromine.[157]



(LXIV) (LXV)

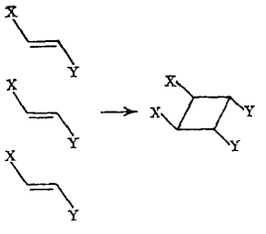
The choice of this particular system was made on the basis of earlier data for gas–crystal reactions and crystallographic studies on olefinic systems; 1,2-asymmetrically substituted crystalline *trans*-olefins interact with bromine vapour to form *erythro*-dibromides as a result of *anti*-addition.[158] Chalcones (αβ-unsaturated ketones) are capable of forming chiral crystals, because their molecules assume highly

twisted conformations in the crystalline state (i.e. the deviation from the achiral planar conformation is large).[159]

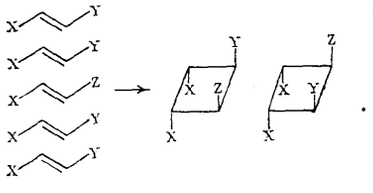
It has indeed been found that the molecules of compound (LXIV), which crystallises in the chiral space group $P2_12_12_1$ have a significantly non-planar structure in the crystal.[160] When ground (in order to increase the area of the exposed surface) crystals of compound (LXIV) are treated with bromine vapour, the dibromide (LXV) is formed with an excess of one of the enantiomers. The optical yield varies from 6 to 25%.[9,157] The determination of the absolute configuration of compound (LXIV)[161] makes it possible to relate the configuration of the initial molecule in the given single crystal to the configuration of the product (LXV) obtained in excess by brominating this single crystal.

It must be emphasised that the optical yield of these gas–crystal reactions depends on the degree of deviation of the molecular conformation from the planar form. This is confirmed by the formation of the racemic dibromide on interaction of bromine with the 4-methoxychalcone (LXVI).[9] Although the crystal of compound (LXVI) is chiral, in this case its molecules deviate less from planarity than in the crystal of compound (LXIV). Studies of the chemical properties and structures of the compounds involved in reactions where bromine adds to racemic crystalline cinnamoyl- and *o*-chlorocinnamoyl-alanines, and of the same compounds after resolution into the individual enantiomers, have also confirmed that the molecular conformation is the principal factor determining the course of these reactions.[9] The optically active dihalides have also been obtained by the addition of chlorine or bromine in the form of monohalogeno-derivatives to compound (LXIV).[9]

We shall consider in greater detail the mechanism of the solid-phase chemical reactions in olefin crystals. When a chiral crystalline olefin, whose molecules are separated by a distance of ~4 Å (β-structure), are irradiated, cyclobutane dimers with *m* symmetry are formed:

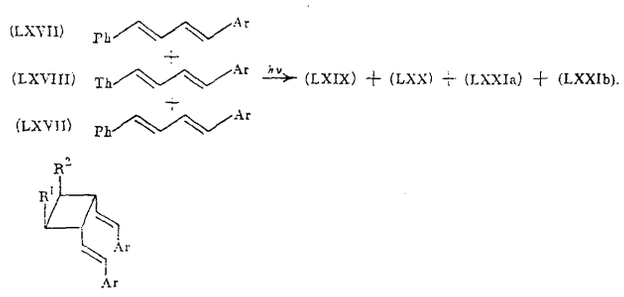


In order to disturb the mirror symmetry, suitable "guest" molecules can be introduced into the "host" lattice. When the correspondence between the molecular geometries of the two components is adequate (solid solutions, mixed crystals), irradiation results in the formation of two enantiomeric "heterodimers" in addition to the two "homodimers", which makes it possible to use these systems for asymmetric synthesis:[9]



To test these hypotheses, phenyl-substituted olefins (stilbenes, 1,4-diarylbutadienes), which form chiral structures, have been used. It has been noted that the necessary intermolecular distance of ~4 Å is attained by the introduction of two chlorosubstituents into the molecules.[3] It is also known that thienyl and phenyl derivatives frequently form mixed crystals.[162,164] In addition, the ability of the thiophen ring to undergo selective excitation in such mixed crystals has been established.[165]

Whereas the crystals of 4-aryl-1-phenylbutadienes (LXVII) and 4-aryl-1-thienylbutadienes (LXVIII) are converted on irradiation into the achiral cyclobutane dimers (LXIX) and (LXX) respectively, having the *m* symmetry, in the (LXVII) + (LXVIII) mixed crystal the enantiomeric heterodimers (LXXIa) and (LXXIb) are formed in addition to the meso-homodimers (LXIX) and (LXX):

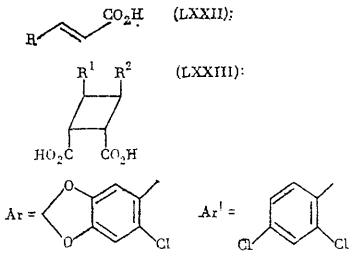



From the standpoint of the elucidation of the influence of the chirality of the crystal structure on the ratio of the enantiomers of compound (LXXI), it is important to excite selectively thienylbutadienes, which absorb in the region of longer wavelengths than the molecules of phenyl derivatives. For small ratios of the concentrations of the thienyl and phenyl derivatives, the selective excitation of the thienyl component suppresses the formation of the achiral dimers (LXIX) and (LXX).

When a light filter is used, irradiation of mixed crystals containing 15% of compound (LXVIII) and 85% of compound (LXVII) at a wavelength of 400 nm leads to a high yield of heterodimers; the filter reduces the absorption by the phenyl derivatives, which prevents the formation of compound (LXIX) and the homogeneous distribution of the thienyl monomer (LXVIII) in the mixed crystal inhibits the formation of the homodimer (LXX). When large homochiral single crystals are irradiated, an optically active dimer is obtained.[57] Dextrorotatory heterodimers are formed in some crystals, while laevorotatory heterodimers are produced in others; the optical yield of these reactions is ~70%. Irradiation at a shorter wavelength ($\lambda < 350$ nm) leads to a decrease of the optical yield, which might have been foreseen by assuming the possibility of absorption by phenyl fragments. This result confirms the preferential propagation of the reaction in stacks, where the distances between the active double bonds are 4 Å.

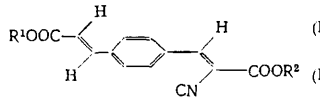
The optical yield of the reaction in the mixed crystal with the ratio (LXVII) : (LXVIII) ≅ 72 : 28[166] is determined by the rate of excitation of the thienyl derivative (LXVIII). Although the translational symmetry of the crystal has been infringed by the substitution of the phenyl group by the thienyl group, the extent of such infringement is slight, as can be seen from X-ray diffraction data, and the intermolecular distances between the olefinic groups in the direction of the ~4 Å translation, are almost identical. The photoexcitation of the thienyl groups can therefore lead to the formation of identical amounts of the enantiomers (LXXIa) and (LXXIb). However, the thiophen fragment is deformed on excitation and the different interactions of the photoexcited compounds (LXVIII) with two nearest neighbours occurring under these conditions induce the appearance of two diastereoisomeric transition states, which explains the observed asymmetry of the synthesis.

The solid-phase reactivity of alkoxyarylchloro-olefins, which also form β-structures, has been investigated.[167] For example, by irradiating at $\lambda \cong 350$ nm the substituted cinnamic acids (LXXIIa) and (LXXIIb), crystallising with formation of the β-structure, it is possible to obtain, as a result of topochemical solid-phase dimerisation, the β-truxillic acids (LXXIIIa) and (LXXIIIb) (with maximum yields of 70 and 90% respectively), compound (LXXIIIb) dimerising much more slowly.[168]




Cyclobutane derivatives of three types [compounds (LXXIIIa), (LXXIIIb), and the chiral compound (LXXIIIc)] are formed on dimerisation in the mixed crystal (LXXIV) made up of compounds (LXXIII) and (LXXII) (in proportions of 1 : 2). The ratios of these reaction products (4 : 1 : 4) agree with the statistical distribution of the molecules of compounds (LXXIIa) and (LXXIIb) in the stack of a (LXXIV) crystal.

Another method of asymmetric synthesis (see above—the chirality of the crystal is determined by the chirality of the molecules of the substance crystallising) requires that the molecules having two different optically active centres be stacked in the chiral crystal in a specific manner—the non-equivalent double bonds must have a favourable disposition (it is required that they be parallel and that the centre–centre distance be ~4 Å) for photocycloaddition with formation of only one of the two possible enantiomers. Among the large number of compounds investigated, 1,4-phenylene diacrylates [for example compounds (LXXV) and (LXXVI)] were selected, since these symmetrically disubstituted compounds are known to be capable of photopolymerisation,[169,170] while chiral s-butyl groups can induce the formation of chiral crystals and can then be readily removed from the product isolated:

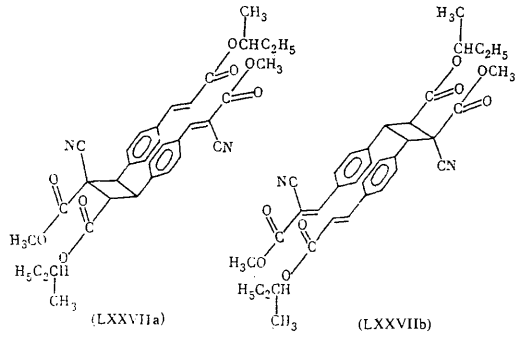



In addition, s-butyl groups ensure a relative disposition of the reacting double bonds at a distance of 4 Å, while the cyano-groups ensure the chirality of the product after the removal of the ester groups.

Two enantiomers of compound (LXXV) [the (*S*)-(+)- and (*R*)-(−)-forms] crystallise in two possible diastereoisomeric forms *A* and $\bar{A}$.[144] The reactions in these crystals lead to the formation of cyclobutane dimers, trimers, and oligomers with identical environments of the $C_4$ rings but with opposite chiralities. The absolute configuration of the molecules in the monomer crystal has been established by X-ray diffraction and the configurations of the dimer, trimer, and oligomers have been determined from the configurations of the molecules of the reacting crystal.

The molecular packing in the crystal of compound (LXXV) agrees with the mechanism of the synthesis examined above. The double bonds of neighbouring translationally linked molecules are separated by 4.04 Å. If one begins with the optically pure (*S*)-(+)-enantiomer of compound (LXXV), then the absolute configurations of its reaction product will be 1*S*, 2*S*, 3*S*, and 4*S*. According to the requirements for the packing of the initial enantiomer, under the conditions of topochemical control, only one diastereoisomer of the dimer, trimer, and the oligomers can be formed. Since the energy difference between structures *A* and $\bar{A}$ is not known beforehand, an independent determination of the diastereoisomeric yield of the products is necessary. Diastereoisomers of type $\bar{A}$ were specially synthesised for this purpose and it was shown that they are absent from the reaction mixture. The dimerising chromophoric groups in the racemate are distributed in the same way as in the enantiomeric crystal.

In the second example of asymmetric induction in an enantiomerically pure monomer, we shall consider the photochemical reaction in the crystal of compound (LXXVI) (space group $P2_1$).[144] The enantiomer of compound (LXXVI) is dimorphous: the α-form is stable under illumination, while irradiation of the (*S*)-(+)-monomer in the β-form, with $[\alpha]_D = +23°$, yields, as a result of the topochemical reaction, the dimer with $[\alpha]_D = +12°$ and the structure (LXXVII).




On the basis of the characteristic features of the packing in the crystal of compound (LXXVI), one may expect the formation of both diastereoisomers—(LXXVIIa) and (LXXVIIb).

It follows from the examples examined that the presence or absence of appreciable asymmetric induction depends on the chiral environment of the reaction centre in the crystal and not on the influence of the chiral s-butyl groups. The quantitative diastereoisomeric yield can be achieved even in the polymerisation of polycrystalline specimens of compound (LXXV) with a low optical purity.[144] The limiting case is the racemic mixture isomorphous with the pure enantiomer but made up of crystals of opposite chirality. Under certain conditions, one may expect the formation of a product having predominantly one chirality and specific rotations up to 30° have indeed been achieved in a number of experiments[126,172] by irradiating large crystals with racemic composition.

These considerations can be extended to any achiral compound belonging to the class of asymmetrically substituted dienes, which crystallise with the same chiral structure as compound (LXXV). The absolute configuration of the products must vary depending on which of the isoenergetic enantiomeric structures is formed on crystallisation. The absolute configuration of the product of the reaction of the enantiomerically enriched monomer (LXXV) is dictated by the chirality of the excess s-butyl groups. Since there is a possibility of the formation of solid solutions of enantiomers, it has been suggested[144] that the system investigated can be used as a solid matrix for the induction of crystallisation of other compounds of this class to give chiral structures.

Irradiation of a solution of 1,6-di-*trans*-cinnamate of (+)-2,3:4,5-di-*O*-methylene-D-mannitol (LXXVIII) leads to the formation of isomeric cyclobutane derivatives as a result of cycloaddition, which can be converted into the stereoisomeric truxillic esters on treatment with methanol. When a crystal of compound (LXXVIII) is irradiated, only intermolecular cycloaddition takes place and dimers, trimers, tetramers, pentamers, and higher oligomers with the α-truxillate cyclobutane unit are formed.[173,174]

The molecule of compound (LXXVIII) has a symmetry close to $C_2$ and the centre of gravity of the molecule has been displaced by 0.3 Å relative to that of the bicyclic fragment.[174] The distance of 3.98 Å between the centres of gravity of parallel C(13)=C(14) and C(17)=C(18) double bonds in the molecules linked by the *b* translation indicates that the condition governing topochemical reactivity is fulfilled for the crystal of compound (LXXVIII).[2]

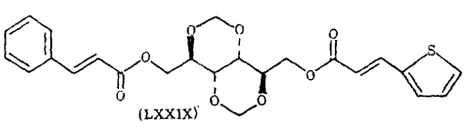
There are no distances permitting interaction between the molecules in the crystal of compound (LXXVIII) extended along the *b* axis, which means that the solid-phase oligomerisation of compound (LXXVIII) should lead to the formation of linear products.[174]

Before the study of Bernstein et al.,[174] the solid-phase di- and oligomerisation was observed only for molecules where two reactive olefinic groups are separated by strictly or approximately planar aromatic ester or amide groups and also by short aliphatic chains.[144,175,176] Bulky groups, such as the tetraoxa-*cis*-decalin group in compound (LXXVIII), had not been used earlier as "spacers" between the reaction centres of solid-phase oligomerisation, just as instances of the presence of 11 covalent bonds between two reactive groups (the distance between the centres of the active double bonds is 13.6 Å) had been unknown. The solid-phase reactivity of compound (LXXVIII) shows that photo-oligomerisation is possible for a much greater number of "spacers" than had been supposed previously. However, it is difficult to predict whether or not the conditions governing the presence of solid-phase reactivity will be maintained: among the six derivatives of D-mannitol with cinnamate end-groups, only compound (LXXVIII) proved to be reactive.[175]

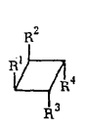
Oligomers (up to octamers) have been isolated chromatographically from the products of the solid-phase photo-oligomerisation of compound (LXXVIII). The proportions of the oligomers depend on the duration of the treatment: brief irradiation promotes the formation of a dimer and short oligomers, while more prolonged exposure entails the appearance of insoluble products, which contain (according to chromatographic data) ten and more monomer units.[174] There exist data indicating further intermolecular photocycloaddition in solutions of oligomers with five and more monomer units.[174,177,178]

In contrast to the crystal, where the molecules of compound (LXXVIII) have the approximate $C_2$ symmetry, in solution this type of symmetry is not characteristic of them according to NMR data and the cinnamate groups are structurally equivalent. Solid-phase photo-oligomerisation enhances the asymmetry and the signals of the cinnamate groups in the NMR spectra of the oligomers are different.[174]

In order to investigate the solid-phase asymmetric synthesis, an attempt has been made to carry out the photo-oligomerisation of compound (LXXIX) tentatively assumed to be isostructural with compound (LXXVIII):[57]



(LXXIX)



(LXXX).

Depending on the relative positions of the molecules in the crystal of compound (LXXIX), the formation of either the enantiomerically pure oligomer (LXXXa) or (LXXXb) [if the structure (LXXIX) is fully ordered] or of the (LXXXa) + (LXXXb) racemate and the achiral product (LXXXc) [for the statistical orientation of the molecules of compound (LXXIX)] might have been expected. However, although the crystals of compound (LXXIX) did exhibit solid-phase activity, they were found to be not isostructural with compound (LXXVIII) and the products of the reactions of compounds (LXXVIII) and (LXXIX) were different. Further work directed towards the investigation of solid-phase solutions of compounds (LXXVIII) and (LXXIX) is being continued.[174]

Racemic derivatives of anthracene frequently crystallise with formation of close-packed enantiomeric pairs of molecules manifesting a characteristic excimer emission and undergoing rapid photodimerisation. The crystals of individual enantiomers have a completely different type of packing, also exhibit a characteristic monomer emission, and are stable as regards the action of light. Esterification with 1-arylethanol of 9-anthroic acid, partly resolved into optical isomers, makes it possible to obtain a mixture of racemic and chiral crystals. On irradiation, the dimer is formed exclusively from racemic crystals. The soluble chiral monomer which failed to react is separated from the insoluble meso-dimer by extraction with hexane; the optical yield reaches 95%.[179]

Optically active products can be obtained from racemic single crystals with the aid of a solid-phase reaction. In principle, it is possible to carry out the reaction only on the upper (or lower) face of such a crystal. The reaction on one face results in the formation of one enantiomer, that on the other affording the other optical isomer. The usefulness of studies on these lines has been confirmed by the difference in the proportions of the reaction products obtained on different single crystal faces[180] and also by the anisotropy of the rate of reaction[181] observed in certain gas–crystal reactions.

The future of the chemistry of organic chiral crystals is associated with the progress in organic solid-state chemistry in general and also with a more profound investigation of the ways in which molecules are packed in crystals. Just as chiral groups are important in the study of many reactions of organic and inorganic compounds in solutions, chiral crystals make it possible to obtain detailed information about solid-phase reactions.

## VI. OTHER REACTIONS

### 1. Chemical Reactions in Clathrate Compounds

Chemical reactions in clathrate compounds are well known (see, for example, Shklover et al.[80]). We shall consider several examples of such reactions. Alkylammonium cations can be incorporated in an inorganic matrix and can form hydrogen bonds with the latter.[182] For example, the intercalation in layer silicates[183] and the formation of mixed crystals by alkylammonium salts with transition metal halides $MX_2$, the so-called "layer perovskites" $(C_nH_{2n+1}NH_3)_2MX_4$, is known.[184,185] There exist numerous data on the magnetic properties and phase transitions in these systems.[186–188] However, until the study of Tieke and Wegner, the possibility of using them as matrices for chemical reactions in the crystal had not been investigated. Tieke and Wegner[182] demonstrated the ability of ω-aminoacids and n-alkylamines to crystallise in "layer perovskites" and also the ability of 6-aminohexa-2,4-dienoic acid, incorporated in $CoCl_2$, $MnCl_2$,

and $FeCl_3$, to polymerise to the *trans*-polyene structure (LXXXI) as a result of solid-phase reactions on irradiation with UV light ($\lambda$ = 254 nm) or $\gamma$-rays:

$$n\,CHR^1{=}CH{-}CH{=}CHR^2 \rightarrow -(-CHR^1{-}CH{=}CH{-}CHR^2{-})_n\ ; \quad (LXXXI)$$

$$R^1{=}CH_2NH_2,\ R^2{=}COOH\ .$$

The polymerisation of *trans,trans*-dienes as a result of 1,4-additon had not been known previously either in the solid phase or in clathrate compounds.[189,190] According to NMR data, the *erythro*-diisotactic disposition of the substituents is postulated in the polymer (LXXXI), which is a racemate. On polymerisation in the clathrate compound in $CoCl_2$, the distance between the layers of metal ions (17.9 Å) increases only by 0.9 Å. The stereoregularity of the products, the insignificance of the structural changes, and the dependence of the reactivity of the monomer on the ionic character of the matrix indicate the possibility of the topochemical control of the reaction.[182] The polymer chains formed as a result of the 1,4-addition of diene groups are extended in the plane parallel to one of the crystallographic directions of the inorganic matrix. The separation of the polymer with an average molecular weight of ~35 000 from the matrix presents no difficulties.[182]

The use of chiral crystals as the medium for asymmetric synthesis is of great interest. This approach makes it possible to "convert" the chirality of the "host" crystal into the chirality of the reaction product.[129,192-195] Among the most successful attempts to carry out such reactions, mention may be made of the solid-phase asymmetric polymerisation of *trans*-penta-1,3-diene (LXXXII) incorporated in the chiral matrix of the crystal of (+)-perhydrotriphenylene.[196,197] $\gamma$-Irradiation results in the formation of an optically active pentadiene polymer, although the molecules of compound (LXXXII) are fixed in the matrix only via van der Waals forces. The same reaction has been carried out in the deoxyfolic acid matrix.[198]

## 2. Topotactic Redox Reactions in Intercalation Systems

Yet another important type of solid-phase reactions involves the formation of intercalation compounds (IC) as a result of the incorporation of "guest" molecules, atoms, and ions in the "host" crystal, which has a suitable structure.[199] Apart from the well known layer systems, for example, graphite, $MoS_2$, and others, both inorganic systems with a skeletal structure (for example $WO_3$) and organic molecular conducting crystals are used for intercalation.[200] The character of the intercalated "guest", ranging from small ions ($H^+$, transition and non-transition metal ions) to large molecular ions (metal complexions, dye, and heterocyclic ions), is also varied.[200]

Direct intercalation can be regarded as a reversible redox electron-ion transfer reaction, which makes it possible to treat from the general standpoint the intercalation processes involving both ions and neutral molecules of the "guest".[200]

Among the fairly varied topotactic redox intercalation processes,[200] the intercalation of organic compounds of the type of Lewis bases (hydrazines, amines, heterocycles, acid amides, *N*-oxides, etc.) in layer dichalcogenides on heating[201,202] as well as the formation of intercalation compounds with molecular "host" crystals[200] are relevant to the subject of the present review.

The interaction of the "host" lattice with the "guest" molecule is usually considered in terms of charge transfer from the donor "guest" molecule to the acceptor—the "host" lattice.[203-206] However, according to latest data, direct intercalation of Lewis bases takes place as a result of topotactic redox reactions with phases having an ionic structure.[207-209] This conclusion has been confirmed by a study of the mechanism of the intercalation of inorganic matrices by ammonia and pyridine. In contrast to the earlier model,[201,211] the $^1H$ NMR data for $TaS_2(NH_3)_x$ and $TiS_2(NH_3)_x$, where $x \cong 1$, indicate the parallel orientation of the $C_3$ axis of the $NH_3$ molecule in the interlayer space of the "host" crystal.[205,206] Such orientation is favourable for interaction with charge transfer between the unshared electron pair of nitrogen and the layers of the $MX_2$ crystal. The study of the mechanism of the intercalation of $NH_3$ has shown that the redox process accompanying this reaction involves the oxidation of some of the "guest" molecules with formation of $N_2$.[209] Electrons pass to the $TaS_2$ layers, while protons are bound to $NH_3$ molecules:

$$2NH_3 \rightarrow N_2 + 6H^+ + 6e^-\ ,$$
$$xe^- + TaS_2 \rightarrow [TaS_2]^{x-}\ ,$$
$$H^+ + NH_3 \rightarrow NH_4^+\ .$$

The intercalated compound $(NH_4^+)_x(NH_3)_{1-x}[TaS_2]^{x-}$ with $x \cong 0.1$ formed has an ionic structure; the $NH_4^+$ cations are "solvated" by neutral $NH_3$ molecules. This scheme accounts for the unusual orientation of the $NH_3$ molecules by the ion–dipole interaction. The thermal intercalation of pyridine (PyH) in $TaS_2$ also takes place as a result of a redox process involving the disproportionation of some of the "guest" molecules with formation of bipyridyl (Py–Py):

$$x\,PyH \rightarrow x/2(Py{-}Py) + xH^+ + xe^-\ ,$$
$$x\,PyH + xH^+ \rightarrow x(PyH_2^+)\ ,$$
$$xe^- + TaS_2 \rightarrow [TaS_2]^{x-}\ .$$

The reaction product also has an ionic structure, namely $(PyH)_{0.5-2x}(PyH_2^+)_x(Py{-}Py)_{x/2}[TaS_2]^{x-}$, where $x \cong 0.2$; the planes of the heterocycles are perpendicular to the six-fold *c* axis of the "host" crystal.[207,210,212]

In the case of compounds with a low ionisation potential, for example, aromatic Lewis bases capable of forming stable radical-cations, the reaction mechanism is simpler; indirect data for this intercalation process involving phenylenediamine have been published.[211] Direct ionisation has been postulated for the thermal intercalation of metallocenes[214,215] as a result of the cathodic reduction of $MX_2$ in electrolytes containing metallocenium cations.[216]

The low electrical conductivity and the low lattice energy prevent the occurrence of topotactic redox processes in molecular crystals. Three cases are exceptions: (a) appreciable intermolecular delocalisation of electrons, for example, as a result of charge transfer or the interaction of the *d* electrons of metals;[217,218] (b) the small size of the "guest" molecules, which leads to an insignificant steric change in the "host" lattice; (c) the presence of convenient ways for the intracrystal diffusion of "guest" ions with low activation energies. The electron-proton transfer is most probable in organic crystals.[200]

Oxygen-transferring metal chelates, for example, [2,2′-ethylenebis-(nitrilomethylidyne)diphenolato]cobalt(2+) and its derivatives have been investigated in greatest detail. These compounds form red-brown crystals, which blacken in air owing to reversible saturation by molecular oxygen.[219-222] Depending on the ligand environment of the cobalt atom, the $Co:O_2$ ratio may be 2:1 or 1:1. Planar chelate complex molecules are packed in such a way that in the crystal there exist large channels open to one-dimensional diffusion of $O_2$ molecules. The $Co^{2+}$ ions are oxidised by oxygen, but the degree of their oxidation has not been established. The chelate complexes of cobalt are used in welding as a source of pure atmospheric oxygen.[200]

Numerous planar metal chelates having an analogous structure with a stacked arrangement of complex molecules are known; their conductivity along the stacks increases sharply on oxidation of the metal ions owing to the interaction with the partly filled *d* orbitals (one-dimensional metals and superconductors). The bis(benzil dioximato)-complexes of nickel(II) and palladium(II) are converted by oxidation with halogens into compounds having the composition $[MR_2]Y$ (Y = Br or I) and a tetragonal structure, characterised by a stacked packing and intermolecular metal–metal interactions; halide ions are distributed in channels parallel to the stack of complex molecules and apparently exist predominantly in the form of the anions $Y_3^-$. The halogen is partly eliminated from the bromo-derivatives, while the tetragonal structure persists over a wide non-stoichiometric range ($z_{max} = 0.8$):[223]

$$[MR_2]^{n+}(Y)^{n-} \rightleftarrows [MR_2]^{(n-x)+}(Y_{1-z})^{(n-x)-} + z/2Y_2\,Y_2 + Y^- \rightleftarrows Y_3^- .$$

Analogous processes are apparently characteristic of partly oxidised phthalocyanines.[224] Phthalocyanines and related metal chelates exhibit an appreciable electrocatalytic oxidative activity in the presence of oxygen,[225,226] which is apparently associated with topotactic redox processes.

Topotactic electron-proton transfer processes have been investigated for tantalum halide clusters and chloroammine-platinum complexes.[227] Reversible electron-proton transfer can occur in crystals of the quinolinium salts of tetracyanoquinodimethane (TCNQ):[228]

$$(C_9H_7NH)^+[(TCNQ)_2]^- + x\,e^- + x\,H^+ \rightleftarrows (C_9H_7NH)^+(H^+)_x[(TCNQ)_2]^{(1+x)-} .$$

Organic molecular crystals with semiconducting properties and an extensive system of π-interactions, for example, dyes and aromatic radical-cations, can be used as electrochromic materials for display purposes.[229–232] Since electron-proton transfer reactions are characteristic of these compounds in solutions,[233] it has been suggested[197] that such processes occur also in the crystalline state. Topotactic doping by oxidants leads to a sharp increase of the conductivity of crystalline polyacetylenes.[234,235]

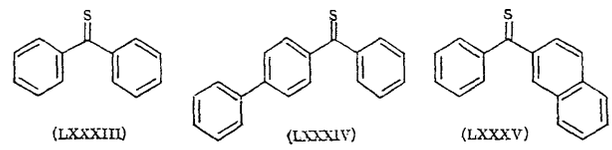
### 3. The Crystal–Gas Interaction

This extremely common type of solid-phase chemical reactions, which hinder the X-ray diffraction of hydrolysable or oxidisable compounds, has been inadequately investigated as regards structure.

One of the examples of the structural investigation of solid-phase reactions of this type, the interaction of chiral single crystals with gaseous bromine leading to chiral products, was examined above (Section V).

Another example of the chemical crystal–gas interaction is provided by topotactic redox reactions in the formation of intercalated systems (see above).

The ability of thioketones to be readily oxidised in solution to the corresponding *S*-oxides or ketones, the rate of oxidation and the proportions of the products being determined by the electronic and steric characteristics of the molecules, is also known.[236] The capacity of thioketones for oxidation in the solid phase is determined by the packing of their molecules in the crystals. The molecules of the aromatic thioketones (V)–(VII), which undergo solid-phase photochemical oxidation, are stacked in such a way that the thiocarbonyl chromophoric groups C=S are oriented in an antiparallel manner (the intermolecular S...S distances vary from 3.70 to 3.90 Å) and form channels along the shortest period of the unit cell.



(LXXXIII) (LXXXIV) (LXXXV)

The cross-sectional area of the channels is ~8.3 Å$^2$ in contrast to the crystals of stable diarylthioketones whose channels are much smaller (~2.3 Å$^2$).[237] The solid-phase reactivity of compounds (LXXXIII)–(LXXXV) can be accounted for by the diffusion of $O_2$ molecules in the channels and by the subsequent oxidation of the C=S groups.[238,239]

The C=S distances in compounds (LXXXIII)–(LXXXV) are 1.61–1.63 Å and are close to the standard C=S bond length in crystals which are stable as regards the photochemical oxidation of thioketones.[237] The solid-phase reactivity of thioketones is apparently not linked directly to changes in the C=S bond length.

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Thus the structural aspect of the solid-phase dimerisation, polymerisation, redimerisation, and other reactions has been investigated for a fairly wide variety of organic compounds. The dimerisation of certain derivatives of 2-benzyl-5-benzylidenecyclopentanone derivatives and the solid-phase polymerisation of diacetylene derivatives take place with rigorous topochemical control at all stages of the reaction with a single crystal → single crystal transition.

At the present time the ideas of crystal engineering have been developed in studies of crystalline low-dimensional semiconductors, metals, and superconductors.[240,241] Crystal engineering merits special consideration as a method of seeking and investigating the properties of this promising class of organic materials (the construction of molecular "corridors" for the preferential migration of electrons, the use of heteroatoms to ensure the overlap of neighbouring molecules, the elimination of the spatial modulation of charge density by altering intermolecular distances, etc.).

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# Surface Phenomena in Nematic Liquid Crystals

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The characteristic features of the surface tension, adhesion, and ordering of the molecules, and their orientation in the surface layers of the liquid-crystal phases of nematogenic compounds in relation to the anisotropic intermolecular interaction have been examined.
The bibliography contains 95 references.

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## I. INTRODUCTION

An understanding of the mechanism of the production of a given orientation of the molecules of liquid crystals between specially treated supports is of considerable practical importance for creating improved electro- and thermo-optical devices based on liquid crystals. The problem has been dealt with to some extent in familiar monographs.[1-5] Most studies, however, have been predominantly experimental and empirical in character, and the discussion of the results has been restricted to general physicochemical considerations, borrowed from the physics of the surface phenomena of ordinary liquids. The few theoretical studies have been devoted to specific chemical compounds, and do not claim to be general in their approach.

It therefore seems appropriate to examine the available experimental results (often contradictory) and various existing theoretical models.

## II. BASIC THEORIES OF THE LIQUID-CRYSTAL STATE

Liquid crystals (LC), or anisotropic liquids, are formed by the molecules of organic compounds which have an elongated shape. Like ordinary liquids, nematic LC are characterised by short-range translational order, but there is no long-range translational order; they can form droplets, and can be drawn into capillaries; and different types of flow are produced in them. At the same time, the long-range orientational order in the arrangement of the long axes of the molecules of nematic LC is preserved, although thermal fluctuations partly deflect the molecules from the predominant direction (denoted by the unit vector **n**, which has been called the "director").

The present examination will be restricted to nematic LC (NLC or nematics). For these, the order parameter

$$Q = {}^1/_2(3\langle\cos^2\theta\rangle - 1),$$

has been introduced, where $\theta$ is the angle of inclination of an individual molecule to the director **n**, and the brackets denote averaging over all possible orientations of the molecules in the macroscopic volume of the material. If the long axes of the molecules are arranged randomly, as in an isotropic phase (or in an ordinary organic liquid), $\langle\cos^2\theta\rangle = 1/3$ and $Q = 0$. The value $Q = 1$ corresponds to 100% parallel mutual orientation of the molecules. In practice, $Q$ can take values of 0.3–0.4 at a temperature close to the transition point from the nematic to the isotropic phase $T \cong T_c$.

The order parameter $Q$ appears in the expression for the total free energy of the liquid-crystal phase, and it is used to describe phase transformations and the changes in the optical, electrical, and magnetic properties of LC with change in temperature. The parameter $Q$ naturally retains its importance in the description of surface phenomena. A typical curve giving the temperature dependence of $Q$, obtained from magnetic susceptibility measurements, is shown in Fig.1.

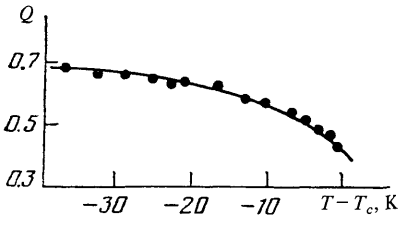



Figure 1. Temperature dependence of the order parameter in the nematic phase of p-azoxyanisole.[4]

In addition to the nematic phase, there exist a large number of other liquid-crystal phases, of which the smectic *A* phase must be mentioned. In it, the molecules are grouped in layers, and the long axes of the molecules are approximately perpendicular to the plane of the layer. The layers can move relative to one another, and the molecules within a layer have short-range translational order. In a nematic phase obtained after heating a smectic LC, clusters with smectic order (or cybotactic groups) are preserved.

For experimental studies, an LC specimen is placed between two glass plates subjected to special treatment. The molecules in the thin layers of the LC are oriented under the influence of the walls of the cell, leading to the formation of the required structures. Rubbing the glass (with paper or diamond paste), the production of a special relief on the glass by applying coatings with an obliquely incident beam, or the deposition of a stepped lattice (by photolithography) create a unique direction in the NLC layer, along which the director **n** is oriented. This direction is called the axis of easy orientation, or the "easy" axis. The methods of treating the support described above lead to the orientation of the director **n** parallel to the support (for example in the direction of rubbing). In the case of thoroughly cleaned glass surfaces or plates covered with surface-active substances, the axis of easy orientation is arranged at right angles to the surface of the support. Thus the orientation of the director close to the support depends on its treatment; the influence of the support extends into the bulk of the specimen, creating a uniform "single-crystal" state (from the viewpoint of optics, nematic crystals behave as monoaxial crystals, whose optical axis coincides with the director **n**). As a result, in a thin layer of LC between treated plates, one of three possible uniform textures is produced: planar with parallel orientation of the molecules with respect to the support, homeotropic with normal orientation of the molecules, or tangential with sloping orientation; the latter exists in the case of a complex relief on the support. The orientation of the director **n** within a specimen relative to the support is generally described using a system of coordinates with the $z$ axis at right angles to the plane of the plates; the $x$ axis is usually directed along the projection of the director **n** (for parallel and sloping orientations).

Table 1. The surface tension of various nematic LC.[10]

| Compound | $\gamma$, erg cm$^{-2}$ | $T$, °C | Method | Refs. |
|---|---|---|---|---|
| MBBA | 38 | 23 | — | [11] |
| MBBA | 35.8 | — | I | [12] |
| MBBA | 30 | — | II | [13] |
| MBBA | 35.3 | — | — | [14] |
| PAA | 38 | 125 | III | [15] |
| PAA | 37 | 120 | — | [14] |
| PAP | 31.2 | 145 | III | [15] |
| 5CB | 28.1 | 31.5 | II | [8] |
| 5CB | 27.9 | 20 | II | [8] |
| 8CB | 26.2 | 41 | II | [8] |

Notes: I—pendant drop method, II—measurements using a Wilhelmy plate, III—capillary rise method; the dash indicates that the method or the temperature of the specimen were not given. Compounds: MBBA = methoxybenzylidenebutylaniline, PAA = *p*-azoxyanisole, PAP = *p*-azoxyphenetol, 5CB = 4-pentyl-4′-cyanobiphenyl, 8CB = 4-octyl-4′-cyanobiphenyl.

Various external influences bring about orientational deformation, associated with the rotation of the local director $\mathbf{n}(x, y, z)$, leading to an increase in the elastic component of the free energy $F_d$. In a magnetic field, for example, the molecules are oriented in the direction of the field **H**. The orientation in an electric field **E** depends on the sign of the dielectric anisotropy $\varepsilon_a$ of the specific LC. Various forms of orientational deformation have been described in detail.[1-5]

Close to the free surface of a liquid-crystal layer (in the case of a freely suspended film or drop on a support), different orientations of the director relative to the normal **N** to the free surface are produced for different substances. For example, for nematic *p*-azoxyanisole (PAA), the angle $\psi$ between the normal **N** and the director **n** on the free surface is 90°,[6,7] whereas for nematic materials of the series of 4-$C_nH_{2n+1}$-4′-cyanobiphenyls, $\psi = 0$.[8] For methoxybenzylidenebutylaniline (MBBA) and ethoxybenzylidenebutylaniline (EBBA), the angle $\psi$ changes with change in temperature.[6,9]

## III. THE SURFACE TENSION OF LIQUID-CRYSTAL MATERIALS

### 1. Experimental Data

The magnitude of the surface tension $\gamma$ for the free surface of the nematic and isotropic phases of liquid-crystal compounds has been measured by different methods at various temperatures. The values of $\gamma$ for individual temperatures are given in Table 1.

The temperature dependence of the surface tension for a given substance, obtained by different authors, often shows lack of agreement, and differences are observed not only in the magnitude of the surface tension, measured at the same temperature by different methods, but also in the nature of the change in $\gamma$ in the region of the phase transformation from the nematic to the isotropic phase (Fig. 2).

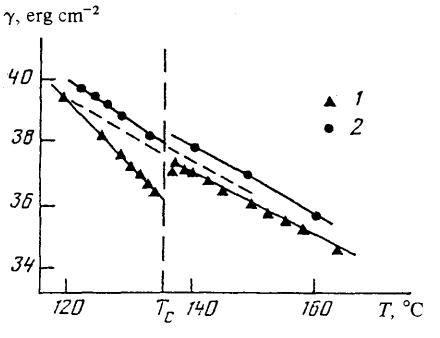



Figure 2. Temperature dependence of the surface tension of PAA, measured by the capillary rise method (*1*),[15] the ring lifting method (*2*),[16] and the maximum gas-bubble pressure method (broken line).[17]

The observed differences in the experimental data are apparently due to differences in the degree of purification of the materials, but the choice of the method used to determine the surface tension also has an extremely significant influence on the results of the experiments; this can be seen, in particular, for the case of PAA (see Fig. 2). In spite of the considerable differences, the curves nevertheless demonstrate important characteristic features of the $\gamma(T)$ relationship for PAA; at a distance from the transition point $T_c$, $\gamma$ changes approximately linearly with increase in the temperature of both the nematic and the isotropic phases; in the region of the transition, the linearity of $\gamma(T)$ breaks down to some extent (depending on the method of measurement); $\gamma$ increases smoothly or abruptly. A

similar non-smooth $\gamma(T)$ relationship in the region of the phase transformation was obtained by the pendant drop method under equilibrium conditions for PAA (Fig. 3*a*) and *p*-anisaldazine (Fig. 3*b*), and also for MBBA.[18]

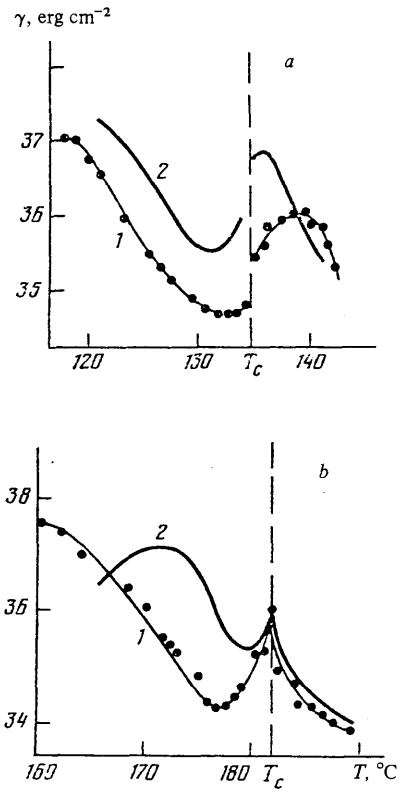



**Figure 3.** Temperature dependence of the surface tension of *p*-azoxyanisole (*a*) and *p*-anisaldazine (*b*):[18] *1*) experiment (pendant drop method), *2*) theoretical curves.[34]

For both MBBA [19] and PAA,[17] the maximum gas-bubble pressure method gives a linear decrease in $\gamma$ with increase in temperature in both phases; on going from the nematic to the isotropic phase, $\gamma$ undergoes a positive jump for both substances.

When the method of detachment (of a plate or ring) from the free surface is used for PAA [16] and MBBA,[20] a linear decrease in $\gamma$ with increase in $T$ is observed, and there is no unique feature (jump) in the region of the transition. Measurements by the Wilhelmy method in an experiment of the continuous type gave $\gamma = 35.0 \pm 0.2$ erg cm$^{-2}$ for MBBA at $T = T_c$.

The same method (Wilhelmy plate), however, gave an appreciably non-linear $\gamma(T)$ relationship close to $T_c$ for 5CB and 8CB.[8] The measurements were made under conditions close to equilibrium, and the rate of displacement was 5–50 mdyne cm$^{-1}$ per day. Measurements with a good accuracy were achieved in this way; for example, for 6CB, $\gamma = 28.1 \pm 0.3$ erg cm$^{-2}$ at 31.5 °C. $\gamma$ increases with increase in temperature, both below and above $T_c$ (Fig. 4). The slope of the $\gamma(T)$ curve is positive close to $T_c$ in both phases (Fig. 4*a*). The maximum on the curve (Fig. 4*b*) was calculated theoretically.[8]

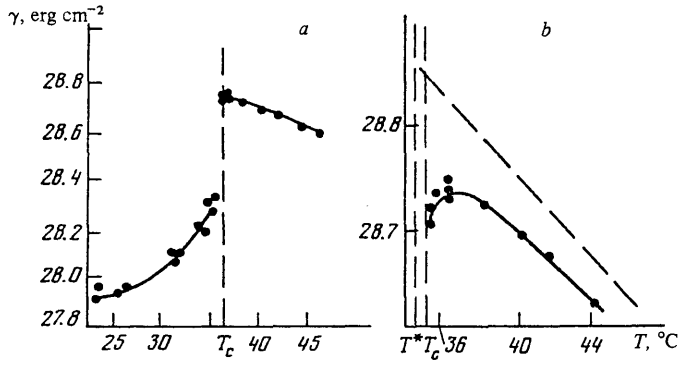



**Figure 4.** Temperature dependence of the surface tension for 5CB in the nematic and isotropic phases (*a*) and in the isotropic phase on an expanded scale (*b*).[8] The thick line gives the theoretical curve, and the broken line the values of $\gamma(0)$, extrapolated from the distant isotropic range.

The fundamental importance of ensuring equilibrium conditions for the reliable determination of $\gamma(T)$ can be proved indirectly for the method involving light scattering from the free surface, in which the shear viscosity and the surface tension are measured simultaneously by generating surface waves and studying their characteristics. The scattering of light from the thermal fluctuations (~10 kHz) of the free surface of MBBA made it possible to calculate $\gamma$ with a relatively low accuracy[21] (Fig. 5*a*). Low-frequency ($\lesssim$1 kHz) running surface waves with a relatively high amplitude (~100 Å) have been used;[22] the temperature dependence of $\gamma$ obtained for the nematic and smectic phases of *p*-cyanobenzylidene-*p*-octyloxyaniline (CBOOA) is shown in Fig. 5*b*. Similar values for the nematic phase of CBOOA were obtained from an experiment on light scattering on the thermal fluctuations of the free surface.[23] It was concluded that within experimental error, $\gamma$ remains constant within the nematic phase; this does not agree with other data.[17,18,34]

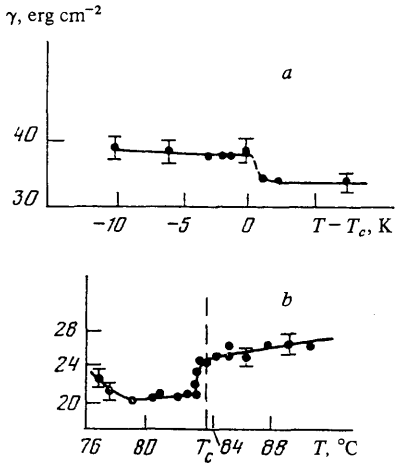



**Figure 5.** Temperature dependence of the surface tension, obtained by light scattering on surface waves: *a*) MBBA in the region of the transition from the nematic to the isotropic phase,[21] *b*) CBOOA in the region of the transition from the nematic to the smectic phase.[22]

The spectra of the autocorrelation functions of surface waves of low amplitude were recently studied and used to calculate the surface tension of PAA.[24] The large scatter in the experimental points (uncertainty ±1 erg cm$^{-2}$) makes possible only a crude estimate, $\gamma \cong 36$ erg cm$^{-2}$, throughout the range of existence of the nematic phase studied.

Thus the non-equilibrium surface-wave method gives values of $\gamma$ with a fairly high uncertainty, so that it is practically impossible to determine the temperature dependence of $\gamma$.

## 2. Theoretical Models of the Surface Tension of Liquid Crystals

Existing calculations of the surface tension $\gamma$ and its temperature dependence have been carried out only for the limiting cases of the orientation of the director next to the phase interface, that is for $\psi = \pi/2$ and $\psi = 0$.

The surface tension $\gamma$ at the free surface of a liquid-crystal material whose molecules are joined by van der Waals interaction has been calculated.[25] The degree of order $Q$ and the angle of inclination of the director $\psi$ do not appear in explicit form in the expression for the interaction potential. In the macroscopic approximation, in which the material is regarded as a continuous medium, it was assumed[25] that two semi-circumferential volumes of the given substance interact with one another through a vacuum gap of thickness $l$. The specific (per unit area of the surface) additional energy of the system due to the van der Waals interaction will then have the form:

$$U(l) = \frac{\hbar}{4\pi}\int_0^{\infty} d\omega \int_0^{k_c} k\, dk \ln[1 - \Delta^2(i\omega)] \exp(-2kl)$$

Here, $k$ is the wavenumber; $\omega$ the frequency of the electromagnetic field; $k_C$ the limiting wavenumber of the fluctuating electric field, directed parallel to the surface; and

$$\Delta(\omega) = [\varepsilon(\omega) - 1]/[\varepsilon(\omega) + 1],$$

where $\varepsilon(\omega)$ is the complex dielectric constant of the liquid.

It is assumed that the free energy $U(\infty) = 0$. Decrease in the gap $l$ to zero gives the quantity $U(0)$, which is equal to the work of cohesion with sign reversed. Thus the free energy of each of the two surfaces is equal to

$$\gamma = -{}^1/_2 U(0)$$

A calculation carried out according to this scheme for the free energy of an isotropic liquid[26,27] gave the following expression:

$$\gamma = -\frac{\hbar}{16\pi^2} k_c^2 \int_0^{\infty} d\omega \ln[1 - \Delta^2(i\omega)]$$

This method can be extended to nematic liquids, taking account of the fact that the dielectric constant of the interacting media is an anisotropic quantity. A rectangular system of coordinates with $z$ axis perpendicular to the surface is used. The dielectric constant of the NLC will then be described by the tensor:

$$\varepsilon(\omega) = \begin{pmatrix} \varepsilon_x(\omega) & 0 & 0 \\ 0 & \varepsilon_y(\omega) & 0 \\ 0 & 0 & \varepsilon_z(\omega) \end{pmatrix}$$

The components of the complex dielectric constant parallel to and perpendicular to the director will be denoted $\varepsilon_\parallel(\omega)$ and $\varepsilon_\perp(\omega)$. In this case, for parallel orientation of the director on the free surface,

$$\gamma_\parallel = -\frac{1}{2}\frac{\hbar}{16\pi^3} k_c^2 \int_0^{\infty} d\omega \int_0^{2\pi} d\varphi \ln \frac{4[\varepsilon_\parallel \varepsilon_\perp \cos^2\varphi + \varepsilon_\perp^2 \sin^2\varphi]^{1/2}}{[\varepsilon_\parallel \varepsilon_\perp \cos^2\varphi + \varepsilon_\perp^2 \sin^2\varphi]^{1/2} + 1} \qquad (1)$$

where $\phi$ is the azimuthal angle of the orientation of the director relative to the $x$ axis. For the orientation of the director normal to the surface, the oscillating electromagnetic field is directed at right angles to the director, and in Eqn.(1) the angle $\phi$ can be put equal to zero. Thus:

$$\gamma_\perp = -\frac{1}{1}\frac{\hbar}{8\pi^2} k_c^2 \int_0^{\infty} d\omega \ln \frac{4(\varepsilon_\parallel \varepsilon_\perp)^{1/2}}{(\varepsilon_\parallel \varepsilon_\perp)^{1/2} + 1} \qquad (2)$$

In the calculation in Ref.25, the boundary wavenumber was taken as $k_C = 2\pi/10$ Å$^{-1}$. Published data[28] on the complex dielectric constant of PAA, and Eqns.(1) and (2), were used to calculate the values $\gamma_\parallel = 37.8$ erg cm$^{-2}$ and $\gamma_\perp = 44.6$ erg cm$^{-2}$.[25] It can be seen that the lowest surface energy corresponds to the parallel orientation of the director on the free surface. Experiment has in fact shown that PAA molecules are arranged in the surface layer parallel to the free surface,[6,7] and the experimental values of $\gamma$ lie in the range 38–39 erg cm$^{-2}$.[15,17] The surface tension $\gamma$ at the boundary between nematic PAA and glass has been calculated similarly; the value

$$\Delta\gamma_{LS} = \gamma_{LS}(\pi/2) - \gamma_{LS}(0) = 0.36 \text{ erg cm}^{-2}$$

was obtained,[25] that is on a clean glass surface the PAA molecules tend to adopt the perpendicular orientation, in agreement with experiment.[29]

A molecular-statistical theory of the surface tension of liquid crystals was developed[30] by examining the anisotropic paired interaction between the LC molecules. It used a general expression for the surface tension of a polyatomic liquid, previously obtained[31] in a calculation of the dipole–dipole contribution to the surface tension of water at a low vapour pressure. If the interaction potential of a pair of molecules $U_{12}$ depends only on the vector of the centres of mass $\mathbf{R} = \mathbf{r}_2 - \mathbf{r}_1$ ($\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of the centres of mass of molecules *1* and *2*) and the orientation of the molecules relative to the direction of the director $\mathbf{n}$, given by the unit vectors $\mathbf{e}_1$ and $\mathbf{e}_2$, the expression for the surface tension has the form:

$$\gamma = -\frac{1}{2}\int_{-\infty}^{+\infty} dz \int d^3R\, d^3e_1 d^3e_2 \left(Z\frac{\partial U_{12}}{\partial Z} - X\frac{\partial U_{12}}{\partial X}\right)\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{e}_1, \mathbf{e}_2) \qquad (3)$$

(in the system of coordinates $x$, $y$, $z$ where the plane $xy$ coincides with the free surface, and the $z$ axis is directed into the depth of the LC layer). In Eqn.(3), $Z$ and $X$ are the coordinates appearing in the expression for the potentials $U$, and $\rho^{(2)}$ is the binary distribution function, defined in such a way that the quantity $\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{e}_1, \mathbf{e}_2) \cdot d^3\mathbf{r}_1 d^3\mathbf{r}_2$ gives the average number of pairs of molecules present in the corresponding states *1* and *2*. Instead of $\rho^{(2)}$ it is more convenient to introduce the distribution function $g^{(2)}$, such that $\rho^{(2)} = \rho^{(2)} g^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{e}_1, \mathbf{e}_2)$, where $\rho$ is the density of the liquid.

For the calculation of the surface energy of a nematic LC,[30] $U_{12}$ was taken as the van der Waals interaction potential in the form used[32] to describe the phase transformation from the nematic to isotropic phase, with the assumption that the molecules are monoaxial and rod-shaped, and that the induced dipole moments are produced along the long axes of the molecules. For a pair of molecules it is possible to introduce the polar angles $\theta_1$ and $\theta_2$ relative to the director $\mathbf{n}$ in a spherical system of coordinates. All the azimuthal angles of these molecules are equally probable, so that the first averaging is carried out with respect to the azimuthal angles. In accordance with the monoaxial symmetry of the nematic phase, it is possible to introduce an order parameter $Q$ from the distribution function $f(\theta)$ of the single molecule:

$$\theta = {}^1/_2 \int_0^{\pi/2} (3\cos^2\theta - 1)\sin\theta \cdot f(\theta)\, d\theta$$

In the average-field approximation, the distribution function of two molecules with respect to the corresponding angles is $f(\theta_1, \theta_2) = f(\theta_1)f(\theta_2)$. Under these conditions, the binary function $g^{(2)}$ takes the form:

$$g^{(2)}(\mathbf{R}, \mathbf{e}_1, \mathbf{e}_2) = g^{(2)}(R)f(\theta_1)f(\theta_2)$$

Thus Parsons' approach[30] includes the following assumptions: the vectors of the centres of mass **R** are distributed isotropically within the meso-phase, the local correlation between the orientations of the molecules can be neglected, and the distribution function $f(\theta)$ is independent of $z$, that is the order parameter $Q$ has the same value in the bulk and on the surface. The calculation gives the expression

$$\gamma = \rho^2/2 \int\limits_{z>0} d^3R Z g^{(2)}(R) \left[ Z \frac{\partial}{\partial Z} - X \frac{\partial}{\partial X} \right] \langle W \rangle \qquad (4)$$

The quantity $\langle W \rangle$ represents the averaging of the Maier–Saupe potential[32] over all azimuthal and polar angles of the vectors **R** under conditions of cylindrical symmetry (the $z$ axis coincides with the director **n**). Thus

$$\langle W \rangle_{\mathbf{e}_1, \mathbf{e}_2, \mathbf{R}} = -\frac{2\nu}{3R^6} \left[ 1 + \frac{Q^2}{5} \right]$$

where $\nu$ is a constant.

Parsons' calculation leads to the following expressions for the parallel and perpendicular orientations of the director relative to the free surface:

$$\gamma_\parallel = \gamma_0 \left( 1 - \frac{4}{9} Q + \frac{8}{27} Q^2 \right) \qquad (5)$$

$$\gamma_\perp = \gamma_0 \left( 1 + \frac{2}{3} Q + \frac{1}{6} Q^2 \right) \qquad (6)$$

where

$$\gamma_0 = (3\pi\rho^3\nu/4) \int\limits_0^\infty \frac{dR}{R^3} g^{(2)}(R) \qquad (7)$$

According to Eqns.(5) and (6), $\gamma_\parallel < \gamma_\perp$ for all values of $Q$ usually realised in the nematic phase.[30] This means that the molecules of the surface layer should be oriented parallel to the surface. The magnitude of the abrupt change in the surface tension at the temperature of the phase transformation $T_C$ is readily determined from Eqns.(5)–(7):

$$(\gamma_0 - \gamma_\parallel)/\gamma_0 = \frac{4}{9} Q_c - \frac{8}{27} Q_c^2$$

where $Q_C$ is the value of the order parameter of the nematic phase at the transition point. For a typical value $Q_C \cong 0.44$,[2] Parsons' model[30] predicts an abrupt increase in $\gamma$ on going to the isotropic phase, in agreement with the experimental data.[15–17]

An obvious merit of Parsons' calculation[30] is that an analytical expression is obtained for the dependence of the surface tension $\gamma$ on the order parameter $Q$. However, it describes sufficiently correctly only the case of rigorously parallel orientation of the director on the free surface, realised, for example, for PAA.

A theory of surface tension for a nematic liquid has been proposed,[34] taking account of the continuous change in the density of the liquid $\rho(z)$ and in the order parameter $Q(z)$ with increase in the distance from the interphase surface along the $z$ axis (coinciding with the normal to the surface N). The theory[34] is not associated with any dependence of $\gamma$ on the orientation of the director on the free surface. The local order parameter $Q(z)$ reaches the value of the bulk order parameter $Q_\nu$ at a sufficient distance from the surface of the liquid. Because of the mathematical difficulty of the problem, only qualitative $\gamma(T)$ relationships were obtained.[34] Variation of some of the parameters appearing in the theoretical equations makes it possible to obtain satisfactory agreement between the theoretical curves and the experimental data in the region of the phase transformation (see Fig.3). At a distance from the transition point $T_C$, the $\gamma(T)$ curves have a negative slope, and close to $T_C$ the quantity $d\gamma/dT$ may be positive. The model of Ref.34 is described in more detail in Ref.2.

To describe the nematic liquids 5CB and 8CB, for which the long axes of the molecules are perpendicular to the free surface, a theory was proposed[8] in which two order parameters were introduced: in the bulk ($Q_0$) and on the free surface ($Q_1$), and $Q_1 - Q_0 \ll 1$. The surface energy is introduced in the form of an expansion with respect to powers of $(Q_1 - Q_0)$ and $(dQ/dz)$ with coefficients $A$ and $B$ which depend on temperature:

$$\gamma = \gamma_0(Q_0) + \left( \frac{\partial \gamma_0}{\partial Q} \right)(Q_1 - Q_0) + \int\limits_0^\infty \left[ A(Q - Q_0)^2 + B \left( \frac{dQ}{dz} \right)^2 \right] dz$$

The minimisation of $\gamma$ with respect to $Q$ and $Q_1$ leads to the expression

$$\gamma = \gamma_0(Q_0) - (\xi/4B)(\partial\gamma_0/\partial Q)^2$$

where $\xi = (B/A)^{1/2}$. Since no detailed microscopic theory exists, the authors cited[8] introduced a simple linear relationship of the form $\gamma_0(Q) = \gamma_0(0) - \alpha Q$, where $\alpha$ is independent of temperature. This gives the expression

$$\gamma = \gamma_0(0) - \alpha Q_0 - (\alpha^2\xi/4B) \qquad (8)$$

which includes only the "bulk" order parameter $Q_0$.

In the Landau–de Gennes theory,[1] the free energy of a nematic is decomposed in powers of $Q$. A critical temperature $T^*$, corresponding to a phase transformation of the second kind, is introduced, with $T_C > T^*$. Using the average-field approximation and the Landau–de Gennes phenomenological model, the authors cited[8] obtained for the isotropic phase ($T > T_C$):

$$\xi = \xi_c [(T_c - T^*)/(T - T^*)]^{1/2} \qquad (9)$$

For the nematic phase ($T < T_C$) the following relationship was obtained:

$$\xi = \xi_c [(T^{**} - T_c)/(T^{**} - T)]^{1/2} \qquad (10)$$

where

$$T^{**} = T_c + {}^1/_8 (T_c - T^*).$$

Substituting Eqns.(9) and (10) in Eqn.(8) gives the following expressions for the surface energy: in the isotropic phase:

$$\gamma \approx \gamma_0(0) - \beta [(T_c - T^*)/(T - T^*)]^{1/2} \qquad (11)$$

and in the nematic phase:

$$\gamma \approx \gamma_0(0) - \alpha Q_0 - \beta [(T^{**} - T_c)/(T^{**} - T)]^{1/2}$$

where

$$\beta = ({}^1/_2)\alpha(Q_1 - Q_0)_{T=T_c} = \alpha^2\xi_c/4B.$$

The relationship

$$\gamma_0(0) = 28.86 - 0.0023\,(T - T_c)$$

was obtained by extrapolating the values from the range of high temperatures of the isotropic phase (broken line in Fig.4*b*). To calculate the value of $\gamma(T)$ in the isotropic phase from Eqn.(11), the value $T_C - T^* = 0.7$ K [35] was used, and the value of $\beta/\alpha^2$ was taken as 0.65 dyne$^{-1}$ cm [8] (Fig.4*b*). Good agreement was obtained between the experimental values and theoretical curve, but it should be noted that $\beta/\alpha^2$ is essentially an arbitrary parameter. It is also

not clear why the authors cited[8] did not carry out a comparison with experiment for the nematic phase, although the temperature dependence of the order parameter $Q_0(T)$ for 5CB is known.

## IV. THE ENERGY OF ADHESION OF A LIQUID CRYSTAL TO A SOLID SUPPORT

Treatment of the surface of glass supports in different ways leads to the production of different liquid-crystal textures (homeotropic and planar).[29,36,37]

In the examination of the orientational deformation of a liquid-crystal specimen, it is usually assumed[1-4] that the orientation of the director n on the supports remains constant, in spite of the change in the orientation of n in the bulk of the specimen. These boundary conditions correspond to so-called strong or rigid anchoring to the support (infinite energy of anchoring of the LC to the support). In the case of a finite energy of anchoring $W_S$, the molecules on the surface of the support change their orientation, and this is expressed in a rotation of the director (weak anchoring). In the simplest case, the potential of the anchoring forces is introduced[37-40] in the form $W_\theta = B\sin^2\theta_0$, where $B = \frac{1}{2}W_S$.

A fairly large number of studies in which the energy of anchoring was determined experimentally by various methods have now been published. For greater clarity, the orientational effects in LC cells whose nature is influenced by the quantity $W_S$ will be examined separately.

### 1. The Frederiks Transition in an External Field

The Frederiks transition involves the reorientation of LC molecules, having dielectric $\varepsilon_\alpha$ or diamagnetic $\chi_a$ anisotropy, under the influence of an external electric E or magnetic H field.[1-3] Orientational deformation of the entire LC specimen takes place. In the general case, the expression for the elastic orientational energy of the specimen per unit volume has the form:[1]

$$F_d = {}^1/_2K_{11}(\mathrm{div}\,\mathbf{n})^2 + {}^1/_2K_{22}(\mathbf{n}\times\mathrm{rot}\,\mathbf{n})^2 + {}^1/_2K_{33}(\mathbf{n}\times\mathrm{rot}\,\mathbf{n})^2$$

where $K_{11}$, $K_{22}$, and $K_{33}$ are the Frank elastic constants for transverse bending, twisting, and longitudinal bending respectively.

The free energy of an original homeotropic specimen is the sum of the bulk elastic energy, the surface anchoring energy, and the energy due to the influence of an external electric or magnetic field of the following form (in the one-dimensional approximation):[38]

$$F = 2B_\theta\sin^2\theta_0 + {}^1/_2\int_{-d/2}^{+d/2}[K_{11}\sin^2\theta + K_{33}\cos^2\theta]\left(\frac{d\theta}{dz}\right)^2 dz - {}^1/_2\int_{-d/2}^{+d/2}\chi_a H^2\sin^2\theta\,dz$$

Here, $\theta$ is the angle between the director n at an arbitrary point of the specimen and the normal to the supports (the $z$ axis), and d the thickness of the specimen. For strong anchoring, the threshold of the Frederiks transition is given by:[1]

$$H_c' = \frac{\pi}{d}\left(\frac{K_{33}}{\chi_a}\right)^{1/2}$$

The existence of a finite anchoring energy, as calculated in Refs. 38–41, leads to a decrease in the threshold $H_C$, and the $H_C(d^{-1})$ relationship becomes non-linear. For MBBA, the following values were obtained[38,41] for $W_S \times 10^{-3}$ (erg cm$^{-2}$): 11.0 for surface-active substances on glass covered with $In_2O_3$ and 6.1 on clean glass; 5.9 for lecithin on glass covered with $In_2O_3$ and 3.1 on cleaned glass.

In the one-constant approximation ($K_{11} = K_{33} = K$), the calculation of the orientational deformation is simplified,[40] and $H_C$ for the Frederiks transition becomes directly proportional to the quantity $(d + 2\xi)^{-1}$, where $\xi = 2K/B_\theta$ has been called the extrapolation length. The Frederiks threshold in an electric field for weak anchoring of the molecules to the walls of the cell is described by the following equation:[42]

$$V_c = V_c'(1 + 2K_u/W_s d)^{-1}$$

where the threshold for strong anchoring is

$$V_c' = 2\pi(\pi K_u/\varepsilon_a)^{1/2}.$$

The Frederiks transition in an electric field has been studied for 5CB. When ordinary glass supports covered with a layer of lecithin were used, strong anchoring of the LC to the support was detected.[43]

The phase difference of polarised light passing through a cell containing an NLC deformed by a magnetic field has been calculated and determined experimentally.[44] To obtain better agreement between the theoretical curves and the experimental data, a new potential of the anchoring forces was introduced, namely:[44,45]

$$W_\theta = C\cos^2\theta_0 + C_4\cos^4\theta_0$$

In an attempt to reconcile the results obtained experimentally in studies of the Frederiks transition and the flexoelectric effect, a potential for the anchoring forces was introduced[46] in the form of the square of the elliptical sine, where the argument $0 \leq k \leq 1$:

$$W_\theta = \frac{1}{2}W_s\mathrm{Sn}^2(\theta_0, k)$$

Table 2. Coefficients of azimuthal anchoring $B_\phi$ of nematic MBBA to a support.[10]

| Method of producing the relief | $B'_\varphi$, J m$^{-2}$ | $B_\varphi$, J m$^{-2}$ |
|---|---|---|
| Rubbing with diamond paste | $8\cdot10^{-5}$ | $7\cdot10^{-6}$ |
| Depositing $SiO_2$ at an angle of 30° | $5\cdot10^{-4}$ | $10^{-3}$ |
| Depositing a film of trimethylchlorosilane | — | $5\cdot10^{-6}$ |

Notes: $B'_\phi$—calculated from Eqn. (12), $B_\phi$—measured experimentally from the Frederiks transition.

The case of the orientational deformation of an NLC on rotation of the director in the plane $xy$ parallel to the walls of the cell can be considered. In this case the potential of the anchoring forces is given by the expression

$$W_\varphi = B_\varphi\sin^2\varphi_0$$

where $\phi_0$ is the angle of deviation of the director from the axis of easy orientation (the $y$ axis). Rubbing of the glass support, and the oblique deposition of $SiO_2$, were used to obtain a planar texture.[10,47] The magnitude of the azimuthal anchoring coefficient $B_\phi$ was determined from measurements of the rotation of the molecules in a magnetic field oriented parallel to the support.[10] The orientation of the molecules along the direction of rubbing is usually attributed to the geometric factor, that is it is assumed that the orientation of the rod-shaped molecules along the grooves is energetically favourable, since elastic orientational deformation does not take place. For the simplest case of a sinusoidal surface relief with wave vector $q$, rotation of the director in a

position perpendicular to the grooves increases the elastic energy by an amount[47]

$$W(\varphi) = {}^1/_4 KAq^3 \sin^2 \varphi_0 \qquad (12)$$

The experimental values of $B_\phi$ and the values calculated from this equation are given in Table 2. The lack of agreement between the experimental and theoretical values is apparently related to the simplification of describing the surface by a sinusoidal function.

## 2. The Flexoelectric Effect

The flexoelectric effect (FE) is related to the asymmetry of the shape of the molecule (for example the "banana-shaped" MBBA) and its constant dipole moment. When an external electric field is applied, polarisation is produced in the specimen as a result of the deformation of the bend, leading to the stabilisation of the orientational deformation in the cell.[1,2] Since the greatest deviation of the director is observed close to the walls of the cell, the flexoelectric effect is very sensitive to the magnitude of the energy of anchoring of the LC to the support.

The fullest theoretical description of the uniform flexoelectric effect is given in Ref. 48. For symmetrical boundary conditions, the value of the angle $\theta$ (between the director n and the $z$ axis) is equal to

$$\theta = (e_3 + p) E \left( W_s \operatorname{sh} \frac{d}{2\zeta} + \frac{K_{33}}{\zeta} \operatorname{ch} \frac{d}{2\zeta} \right)^{-1} \operatorname{sh} \frac{z}{\zeta}$$

where $e_3$ is the flexoelectric coefficient for the geometry of the experiment described above and the "banana-shaped" molecules of MBBA,

$$\zeta = E^{-1} (4\pi K_{33} / |\varepsilon_a|)^{1/2}$$

the dielectric coherence length, and $p$ the surface polarisation at the boundary between the solid support and the LC (possibly produced as a result of the difference in the values of the interaction of the support with the two different ends of the elongated LC molecule). The induced birefringence of the specimen is calculated from the equation:[49]

$$\Delta n = \frac{1}{4d} n_0 \left( 1 - \frac{n_0^2}{n_e^2} \right) \left( \frac{e_3 + p}{K_{33}} \right)^2 E^2 \zeta^3 \left( \operatorname{sh} \frac{d}{\zeta} - \frac{d}{\zeta} \right) \times \times \left\{ \operatorname{ch}^2 \frac{d}{2\zeta} \left[ 1 - \frac{\zeta W_s}{K_{33}} \operatorname{th} \frac{d}{2\zeta} \right]^2 \right\}^{-1} \qquad (13)$$

In most experimental studies,[49-51] the calculations were carried out using different simplified versions of Eqn. (13); thus $W_S$, $p$, and $\varepsilon_a$ (in different combinations) were neglected; the expansion of the hyperbolic functions in a series with respect to powers of $(d/\xi)$ was carried out only as far as the first or second order of smallness. In fact, the experimental $\Delta n(d, E^2)$ relationship gave the effective flexoelectric coefficient $e_3^*$:

$$e_3^* = \frac{e_3 + p}{1 + dW_s / 2K_{33}} \qquad (14)$$

Eqns. (13) and (14) were used to determine the energy of adhesion between MBBA molecules and a support treated with an aqueous solution of decyltrimethylammonium bromide.[49] The value was $3.74 \times 10^{-3}$ erg cm$^{-2}$ in a cell with a thickness of 30 μm for $T_C - T = 16$ K and $2.48 \times 10^{-5}$ erg cm$^{-2}$ for a thickness of 90 μm and $T_C - T = 4.5$ K.

These results indicate that the energy of anchoring depends markedly on the temperature of the specimen. Nevertheless, order of magnitude agreement ($10^{-3}$ erg cm$^{-2}$) is observed with the data obtained from the Frederiks transition.[38,41]

## 3. The Spontaneous Frederiks Transition

In nematics with negative dielectric anisotropy ($\varepsilon_a < 0$), the effect of spontaneous breakdown of the homeotropic orientation at a certain critical thickness of the layer is observed.[52] This effect can be attributed[53] to polarisation in the regions of the homeotropic nematic next to the surface, and hence to an electric field $E_S$ existing in a region of thickness $\delta$ next to the surface. A new term is therefore introduced into the expression for the free energy of the specimen to take account of the energy next to the surface

$$(\varepsilon_a E^2 \delta / 4\pi) \sin^2 \theta_0.$$

Solution of the corresponding equations[53,54] shows that there exists a certain critical cell thickness

$$d_c = 2K | W_s + \varepsilon_a E_\delta^2 / 4\pi |^{-1}.$$

For $d < d_C$, the layer is energetically more favourable in the non-deformed state; for $d > d_C$, on the other hand, the layer is deformed according to the law $\theta = \theta_C = (z - d/2)$. Thus the mechanism of the spontaneous transition is attributed[54] to competition between electric forces of different character next to the surface, facilitating planar orientation of the nematic with $\varepsilon_a < 0$, and the elastic energy of the NLC, which favours the homeotropic orientation. This effect obviously decreases the threshold of the ordinary Frederiks transition.

The orientation of an NLC is influenced considerably by long-range dispersion forces,[46,55] which often stabilise the homeotropic orientation of the director. A theoretical examination of a one-dimensional stabilising field has been carried out.[56] At a layer thickness $d < d_1$, the predominating van der Waals forces lead to homeotropic orientation on the surface of the nematic layer; for $d_1 < d < d_2$ the planar orientation on the surface is ensured by short-range surface forces with a potential $\gamma \cos^2 \theta_0$; for $d > d_2$, the most important role is played by the elastic energy of orientational deformation.[55]

Theoretical calculations[57,58] have shown that shielding of the supports by amorphous films with thickness $l$ leads to a local Frederiks transition in the NLC close to the boundary with a support. The moment of the van der Waals forces is described by the expression

$$\lambda c \sin \theta_0 \cos \theta_0 / (\lambda + z + l)(z + l)^2,$$

where $c$ is a constant, and $\lambda \cong 1000$ Å, and the moment of the short-range surface forces has the form $W_S \sin \theta_0 \cos \theta_0$. An experimental study of a local Frederiks transition was carried out[59] on fragments of crystalline mica with a shielding covering in the form of stepped monolayers of stearic acid. The mica support produces planar orientation of the NLC, and the Langmuir layers produce homeotropic orientation, so that for a Langmuir film of sufficient thickness, a change from planar to homeotropic texture is observed experimentally for liquid-crystal droplets of MBBA and 5CB.

# V. THE SURFACE ORDER PARAMETER

The order parameter $Q$ is an important characteristic of the meso-phase, and is widely used to describe the temperature dependence of various physical characteristics of LC.[2,4] It may be assumed that the values of $Q$ in the volume of a specimen ($Q_V$) and close to a solid support ($Q_S$) are different. This assumption has a significant effect on the calculation of the surface properties of liquid crystals, so that a number of attempts have been made to determine the surface order parameter experimentally.

The first estimates of $Q_S$ and $Q_V$ for planar nematic textures[60,61] were made by multiple-wave interferometry.[62] It was assumed[60] that in the region of solid supports, surface forces produce layers with a surface order parameter $Q_S$ (and corresponding refractive index $n_S$), which have a thickness of the order of the wavelength of light. The cell therefore forms a Fabry–Perot interferometer, but with a three-layer optical medium ($n_S$, $n_V$, $n_S$). The ratio of the intensities of the emergent and incident light beams is given by:[60]

$$\frac{I}{I_0}=\frac{8n_p^2n_s^2}{(n_p^4+6n_p^2n_s^2+n_s^4)-(n_p^4-2n_p^2n_s^2+n_s^4)\cos^2\beta}$$

where $\beta = \pi\bar{n}d/\chi$, $\bar{n}$ is the average value of the refractive index in the volume of the specimen, and $n_p$ the refractive index of the glass plate supports. Increase in temperature leads to changes in the values of both $n_S$ and $\bar{n}$, so that the periodic change in $(I/I_0)$ with increase in temperature makes it possible to determine the value of $\bar{n}$ from the phase, and of $n_S$ from the amplitude of the graph.

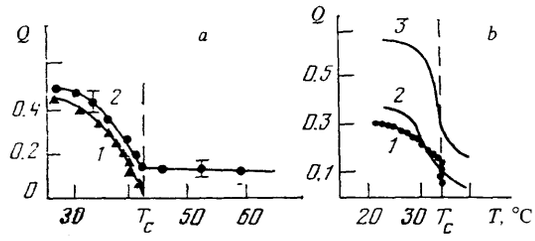



Figure 6. Temperature dependence of the bulk (curves *1*) and surface (curves *2* and *3*) parameters, measured for 7CB [60] (*a*) and 5CB [61] (*b*). Curves *2* were obtained for a support with a layer of $SiO_2$ deposited at an angle of 60°, and curve *3* for a profiled support with a rectangular lattice period of 0.5 μm.

The temperature dependence of $Q_V$ and $Q_S$ obtained by this method[60,61] is shown in Fig. 6. For a specimen of 7CB in a cell with a coating of $SiO_2$, applied at an angle of 60° to the normal, the value of $Q_S$ is slightly greater than $Q_V$, but does not become zero after the phase transformation into the isotropic phase (where $Q_S \cong 0.1$).[60] A much higher value of $Q_S$ compared with $Q_V$ is observed for 5CB for a surface with a profile in the form of a grid with rectangular projections.[61] The authors themselves[61] mention the experimental difficulties associated with this type of interference method for determining $Q_S$. Measurements of the refractive indices $n_\perp$ in planar cells containing MBBA and 5CB have been carried out[63] by two methods: by total internal reflection and by multiple-wave interferometry, and the results obtained by the two methods agreed within the experimental error. This indicates an extremely small difference between $Q_S$ and $Q_V$ in these experiments or a small thickness of the boundary layer ($\xi \ll \lambda$).

A number of published papers[64–68] describe the birefringence in the isotropic phase of nematic compounds, produced by the influence of previously treated supports. To obtain planar orientation of the molecules, the glass plates were rubbed with paper, or covered with surface-active substances (for example polyvinyl alcohol) or with a layer of $SiO_2$. The phase difference $\delta$ of the ordinary and extraordinary waves was determined directly by measuring the intensity of the light passing through the cell, placed between two polaroids. The $\delta(T)$ relationships obtained for a number of specimens are shown in Fig. 7.

The values of the phase difference measured in this way make it possible to determine the briefringence $\Delta n$ and then to calculate the parameter $Q_S$. For this purpose, the Landau–de Gennes approximation was used[65,66] to expand the free energy of the system in a series with respect to the order parameter $Q$:

$$F = F_0 + \frac{a}{2}(T-T^*)Q^2 - \frac{b}{3}Q^3 + \frac{c}{4}Q^4 + \frac{L}{2}|\nabla Q|^2$$

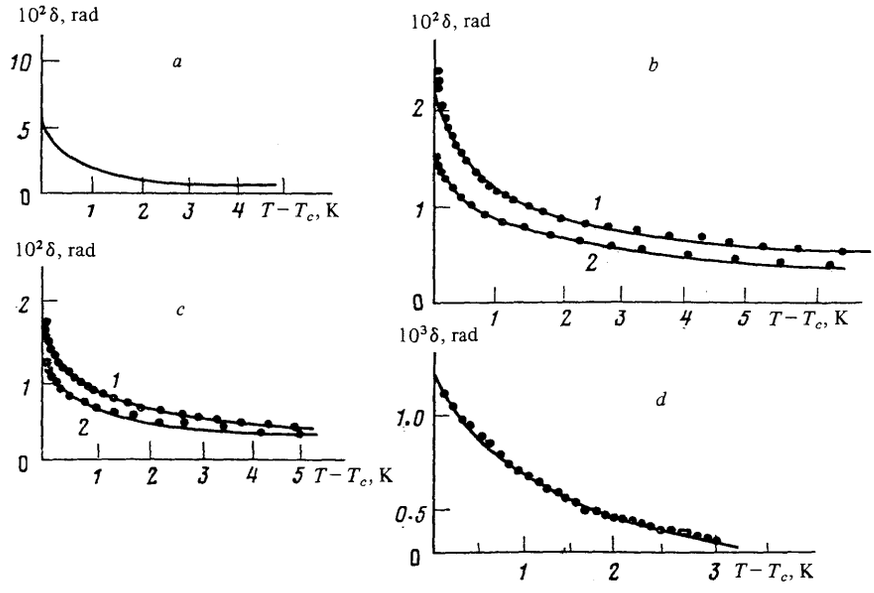



Figure 7. Experimental phase difference relationships $\delta(T)$ in specimens of isotropic nematogenic compounds: *a*) MBBA on glass covered with a rubbed layer of PVA; [66] *b*) 5CB on rubbed glass (*1*) and on a rubbed layer of MAP (*2*); [65] *c*) 5CB on glass covered with HTAB (*1*) and MOAP (*2*); [65] *d*) 7CB on rubbed glass (Pyrex) [67] (the notation for the SAS is explained in the notes to Table 3).

where the coefficients of the expansion $a$, $b$, $c$ are the critical temperature of the virtual phase transformation of the second kind; $T^*$ were estimated for the compounds studied.[67-69] It was assumed that the order parameter $Q$ in the isotropic phase has a finite value at the boundary with the support $Q_{z=0} = Q_S$ and $Q_{z=\infty} = 0$. Minimisation of the free energy with respect to $Q$ incorporating these boundary conditions gives an equation in $Q(z)$:

$$\frac{L}{aT^*}\left(\frac{dQ}{dz}\right)^2 = 2\left[\frac{a}{2}(T-T^*)Q^2 - \frac{b}{3}Q^3 + \frac{c}{4}Q^4\right]/dT^*$$

This equation is solved numerically for various known[67-69] values of $a$, $b$, $c$, and $T^*$ and a reasonable value of $L$. The $Q(z)$ graph obtained is used to calculate $Q_S$. The area under the curve is equated to the value of the birefringence $\Delta n$ induced by the support. The values of $\Delta n$ calculated for different values of $Q_S$ are compared with the experimental value to obtain the order parameter $Q_S$ "next to the wall" for each experiment (see Table 3).

Table 3. Order parameter $Q_S$ "next to the wall"[65,66] in an isotropic phase.

| Method of treating the surface | MBBA | 5CB |
|---|---|---|
| Cleaning | 0 | 0 |
| Cleaning and rubbing | 0.052 | 0.22 |
| Coating of HTAB | 0.321 | 0.32 |
| Coating of MAP and rubbing | 0.063 | 0.18 |
| Coating of DMOAP | 0.054 | 0.17 |
| Depositing $SiO_2$ at an angle of 60° to the normal | — | 0 |
| Coating of PVA and rubbing | 0.364 | 0.172 |

Note. The following substances were used as surface-active substances for treating the surface of the glass support: for the normal orientation—hexadecyltrimethylammonium bromide and its 0.2% solution in chloroform (HTAB) and dimethyl-n-octadecyl-3-aminopropyltrimethoxysilane chloride (DMOAP); for the parallel orientation—N-methyl-3-aminopropyltrimethoxysilane (MAP), polyvinyl alcohol (PVA). Rubbing the surface already covered with SAS gave the planar orientation required to produce an axis of easy orientation in the plane of the support.

Experimental studies in the same direction were continued[67,68] by measuring $\delta(T - T_C)$ in 7CB (see Fig.7d). The values obtained were $Q_S = 0.1$ for rubbed glass, and $Q_S = 0$ for a layer of $SiO_2$ deposited at an angle of 60°. Without treatment of the glass, in the presence of a magnetic field $H$ parallel to the glass surface, birefringence appears as a result of the orientation of the molecules of the isotropic phase by the magnetic field. When the magnetic field is switched off, the birefringence is preserved, that is the field plays the same role as rubbing; a direction of easy orientation is created in the plane of the support.

The birefringence induced by a support was measured[70] in the isotropic phase for a mixture of 5CB with the organic compound hexamethylbenzene (2.5 mole %) on supports covered with a rubbed film of PVA and a deposited layer of $SiO_2$. The surface order parameter $Q_S$ had the values 0.27 and 0.005 respectively.[70] In those cases where the planar orientation of the nematic phase is induced by geometric factors (deposition of $SiO_2$), there is practically no birefringence in the isotropic phase close to the support.

Similarly, when the homeotropic texture of an NLC is produced by thorough cleaning of the glass, birefringence is not produced in the isotropic phase. Thus the birefringence (and hence the ordering) induced by the walls is apparently due to an anisotropic physicochemical interaction between the molecules of the nematogenic material and the support. The absence of ordering in the isotropic phase detected[65-68] when $SiO_2$ was deposited does not agree with other studies[60,61] in which a high value of $Q_S$ on supports of this kind was reported.

Birefringence is also produced in strongly polar organic liquids close to the solid walls of the cell, and the optical axis is perpendicular to the surface of the glass supports. This birefringence is related to an order parameter $Q_S$, in spite of the fact that the liquids studied (nitrobenzene, etc.) do not have a liquid-crystal phase. It has been suggested that a layer of ordered liquid with properties similar to those of a nematic phase is produced close to the surface of the support.†

## VI. ORIENTATION OF THE DIRECTOR ON THE FREE SURFACE OF A NEMATIC LIQUID CRYSTAL

Various optical methods have established that the director **n** on the free surface of an NLC is directed parallel to the surface in PAA,[6,7] and perpendicular to it in cyanobiphenyls,[8,9] and that the angle $\psi$ between the director **n** and the normal **N** to the surface changes with change in temperature in MBBA and EBBA.[6,9] Thus the direction of the axis of easy orientation on the free surface depends on the nature of the liquid-crystal compound.

Accurate measurements of the angle $\psi$ are possible only in uniform specimens: this is usually achieved by applying a magnetic field **H** at a small angle to the free surface. The axis of easy orientation then lies in a plane parallel to **H** and **N**. The magnitude of the relative coefficient of reflection of polarised light incident at small angles (~0.2°) to the normal has been determined experimentally:

$$R = (\rho_\parallel - \rho_\perp)/\rho_\perp$$

where $\rho_\parallel$ and $\rho_\perp$ are the reflection coefficients of light polarised parallel to and perpendicular to the plane of incidence of the light:[7]

$$\rho_\perp = \left(\frac{n_\perp - 1}{n_\perp + 1}\right)^2$$

$$\rho_\parallel = \left(\frac{n(\psi) - 1)}{n(\psi) + 1}\right)^2$$

$\psi$ has been calculated[9] using the following expressions:

$$\rho_\parallel = \left[\frac{(n_\perp^2 \sin^2\psi + n_\parallel^2 \cos^2\psi)^{1/2} - n_\perp n_\parallel}{(n_\perp^2 \sin^2\psi + n_\parallel^2 \cos^2\psi)^{1/2} + n_\perp n_\parallel}\right]^2 \qquad (15)$$

$$\rho_\perp = \left[\frac{n_\perp - 1}{n_\perp + 1}\right]^2$$

It was found that throughout the entire range of existence of nematic PAA, the molecules are arranged so that their long axes are parallel to the free surface, to within 3%.[7] For MBBA and EBBA, Eqns.(15) were used to calculate the temperature dependence of the angle $\psi$ (Fig.8). In a short temperature range close to the phase transformation (from $T_C$ to $T_C$ + 2 °C), the following relationship holds well:[9]

$$\psi = C(T_0 - T)^\beta$$

†See B.V.Deryagin, Yu.M.Popovskii, and B.A.Altoiz, J.Coll.Interface Sci., 1983, **96**, 492.

where for MBBA, $T_0 - T_C = -(0.9 \pm 0.3°)$, $\beta = 0.50 \pm 0.04$, $C = 14.5 \pm 0.6$ degree$^{-1/2}$; for EBBA, $T_0 - T_C = -(1.2 \pm 0.3)$ °C, $\beta = 0.51 \pm 0.1$, $C = 11.8 \pm 1.6$ degree$^{-1/2}$. Above the critical temperature $T_0$ (but below the point of the transition to the isotropic phase $T_C$), the angle $\psi = 0$.

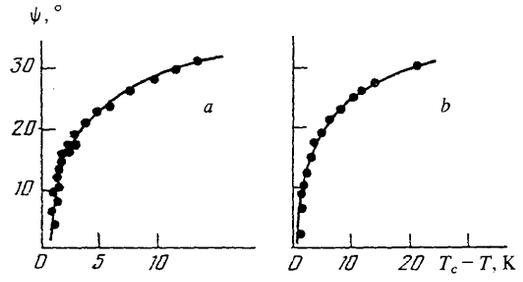



Figure 8. Temperature dependence of the polar angle $\psi$ at the free surface of MBBA (*a*) and EBBA (*b*).[9]

Qualitatively similar results were obtained for free MBBA films[71] in the absence of a magnetic field. The angle of inclination $\psi$ was measured from the conoscopic picture of individual uniform regions of the film; a convergent beam of laser radiation was passed through the specimen and the analyser. At a thickness $d > 70$ μm, the specimen was non-uniform; decrease in the thickness led to the production of a homeotropic texture, after which, at $d < 10$ μm, a schlieren texture typical of nematics with an oblique orientation of the director at the boundaries was produced. The angle $\psi$ decreased with increase in temperature, becoming zero at $T_0$ slightly lower than $T_C$.

The temperature dependence of $\psi$ can be explained using the equation proposed by Parsons[30,33,72] for the surface tension:

$$\gamma = \gamma_0 + \frac{1}{2}\gamma_Q (\mathbf{nN})^2 - \gamma_P \mathbf{nN}$$

where the second term describes the increase in the surface tension on the inclination of a director lying parallel to the surface, and the third term describes its simultaneous decrease as a result of the interaction of the dipole moments of the molecules close to the surface. Thus there exists an equilibrium state of the director, determined by the condition for a surface tension minimum:

$$\frac{d\gamma}{d\psi} = -\gamma_Q \sin\psi\cos\psi + \gamma_P \sin\psi = 0$$

from which

$$\cos\psi = \gamma_P/\gamma_Q \quad \text{for } \gamma_P < \gamma_Q$$
$$\cos\psi = 1 \quad \text{for } \gamma_P > \gamma_Q$$

Since $\gamma_P$ and $\gamma_Q$, generally speaking, change in different ways with change in temperature, $\cos\psi$ is a function of temperature, and with the condition $\gamma_P = \gamma_Q$ the oblique texture is converted smoothly into a homeotropic structure. The temperature for this equality apparently corresponds to the experimental value of $T_0$.

In the direct proximity of $T_0$, the surface tension can be represented as a series with respect to powers of $\psi$:[9]

$$\gamma = \gamma_0 + {}^1/_2 A (T - T_0)\psi^2 + (B/4)\psi^4 \qquad (16)$$

For $T < T_0$, $A/B > 0$, and the minimisation of Eqn.(16) gives:

$$\psi = (A/B)^{1/2}(T_0 - T)^{1/2}$$

On the other hand, for $T_0 < T < T_C$, $\psi = 0$. These elementary estimates agree well with experimental data.[9]

The question of the orientation of the director on a free surface has been studied theoretically.[73,74] The specific energy of the oriented layer on the surface was written in a form analogous to that for the energy of an electric or magnetic field:

$$\Lambda_e = -\frac{1}{2}\Delta\pi\left[(\mathbf{nN})^2 - \frac{1}{3}\right]$$

where $\Delta\pi$ plays the role of the anchoring coefficient of the LC to the free surface. It was assumed[73,74] that $\Delta\pi = \Delta\beta Q$, where $Q$ is the nematic order parameter, and $\Delta\beta$ was called the anisotropy of the ordering. High values of $\Delta\pi$ correspond to a strong orienting influence of the surface. The elastic orientational energy of the surface layer was then introduced, where the moduli of elasticity $\bar{K}_1$ and $\bar{K}_2$ differ from the bulk values $K_{11}$ and $K_{22}$. The propagation of this deformation into the depth of the layer leads to an increase in the bulk elastic energy. From these considerations, the author cited[74] obtained an equation for the moments of the forces acting on the director on the free surface, and calculated the temperature dependence of the angle $\psi$ (Fig.9).

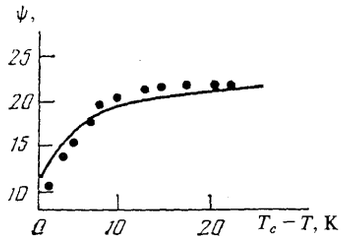



Figure 9. Temperature dependence of the angle between the director **n** and the free surface of MBBA: experiment[6] (points) and calculation (continuous curve).[74]

In all the above studies, $\psi$ was assumed to be independent of the magnitude of $H$, which corresponds to "strong anchoring" of the LC on the free surface. At high values of $H$, however, and at a temperature close to $T_0$, the angle $\psi$ increases with increase in the magnetic field strength.[75] For rotation through an angle $(\psi - \psi_0)$ relative to the original position $\psi_0$ it is necessary to expend the energy of the magnetic field corresponding to the sum of the energy of anchoring of the molecules to the free surface and the energy of elastic deformation in the volume of the NLC adjoining the surface. Thus the total free energy of the surface layer of the LC consists of three terms, and its minimisation with respect to variation of the polar angle $\theta(z)$ in the volume and $\psi$ on the surface gives the equation:[75]

$$\psi \approx \psi_0 + (K_{33}\chi_a)^{1/2}\left(1 + \frac{(K_{11} - K_{33})\sin^2\psi}{K_{33}}\right)^{1/2}\frac{H\cos\psi}{2B_d} \qquad (17)$$

The quantity $\psi(H)$ is calculated from the coefficients of reflection of light $\rho_\parallel$ and $\rho_\perp$. If the temperature dependence of $\psi$, $K_{ii}$, and $\chi_a$ are known, it is possible to obtain from

Eqn.(17) the temperature dependence of the coefficient of adhesion $B_\sigma$ of the NLC molecules to the free surface (Fig.10).

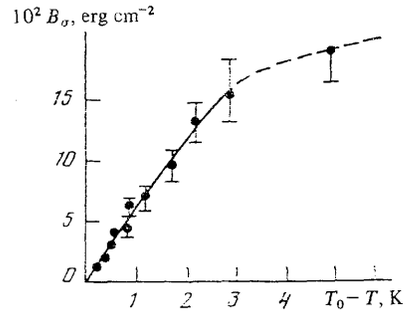



**Figure 10.** Temperature dependence of the coefficient of adhesion $B_\sigma$ to the free surface of MBBA.[75]

## VII. CRITERIA FOR DETERMINING THE NATURE OF THE ORIENTATION OF LIQUID CRYSTALS ON SUPPORTS

The relationship between the surface energy at the phase boundary and the molecular ordering of LC was first explained as follows.[68] For a sufficiently low surface energy of the support $\gamma_S$, the intermolecular forces within the LC are stronger than the forces acting at the phase boundary. As a result, the arrangement of the long axes of the NLC molecules perpendicular to the surface is energetically more favourable. When the surface energy of the solid support $\gamma_S$ is high, the forces of inter-phase interaction predominate, and the NLC molecules are oriented parallel to the support.

Since it is difficult to determine the value $\gamma_S$, for crude estimates it is replaced by the value of the critical surface tension of the support $\gamma_C$, which can be determined by Zisman's method.[76] The procedure for determining $\gamma_C$ by the published method[77] can be described. It is assumed that a drop of liquid with surface tension $\gamma_L$ forms a drop with a contact angle $\alpha$ on a support with energy $\gamma_S$. In this case

$$\gamma_s - \gamma_{sL} = \gamma_L \cos\alpha$$

where $\gamma_{SL}$ is the interfacial surface energy at the boundary between the liquid and the support. Zisman[76] showed experimentally that $\cos\alpha$ decreases linearly with increase in $\gamma_L$ for homologous series of organic liquids. By selecting a series of different liquids with $\gamma_L > \gamma_S$, it is possible to construct the dependence of $\cos\alpha$ on $\gamma_L$ for each support. By extrapolating $\alpha \to 0$ and $\cos\alpha \to 1$, the previous equation is transformed to

$$\gamma_s - \gamma_{sL} = \gamma_c$$

where $\gamma_C$ is determined from the graph for $\cos\alpha = 1$.

The quantity $\gamma_C$ has been called the critical surface tension of the support.

The simple assumption[36,78] that the homeotropic orientation is produced when $\gamma_L > \gamma_C$, and the planar orientation when $\gamma_L < \gamma_C$ gave satisfactory results for MBBA,[12] but was not confirmed for a large number of different NLC on supports covered with surface-active substances (SAS).[79] The molecular ordering was studied in LC of six types on five types of polymer support with $\gamma_C$ in the range 22–40.5 erg cm$^{-2}$. It was found that the lower $\gamma_C$ for the support, the greater the number of LC compounds that undergo homeotropic orientation. For very high values of $\gamma_C$, the planar texture of LC is observed most frequently.[77] For various types of LC and SAS, the ordering can be related to the value of the contact angle of the LC drop: a homeotropic texture is produced for $\alpha \geq 36°$, and a planar texture for $\alpha \leq 36°$.

The surface tension of liquid crystals $\gamma_L$ has been measured at the same temperatures, and amounted to 34.4 erg cm$^{-2}$ for 5CB, 34.2 erg cm$^{-2}$ for MBBA, and 32.6 erg cm$^{-2}$ for dibutyloxyazoxybenzene. Table 4 shows that the condition $\gamma_L > \gamma_C$ is not necessary for the production of a homeotropic texture. Other experiments, however, did not show any characteristic relationship between the ordering and the magnitude of the contact angle[79] (see Table 4).

Table 4. Critical surface tension of the support $\gamma_C$, the contact angles of wetting, and the orientations of the director in liquid crystals on glass supports treated with a solution of 0.5 mass % alkoxysilanes.[79]

| Alkoxysilanes | $\gamma_C$, erg cm$^{-2}$ | 5CB | | MBBA | | Dibutyloxyazoxybenzene | |
|---|---|---|---|---|---|---|---|
| | | $\alpha$, ° | orientation | $\alpha$, ° | orientation | $\alpha$, ° | orientation |
| GMS | 38.5 | 0 | ∥ | 0 | ∥ | 0 | ∥ |
| AAMS | 36.0 | 0 | ⊥ | 0 | ∥ | 0 | ∥ |
| PHES | 32.0 | 16 | ∥ | 15 | ∥ | 8 | ∥ |
| MAP | 29.0 | 16 | ⊥ | 15 | ∥ | 12 | ∥ |
| DMOAP | 23.0 | 55 | ⊥ | 56 | ⊥ | 46 | ⊥ |

Another method of introducing a criterion for the orientation of LC is by representing the surface energy as a function of the angle of orientation $\theta$ at the phase boundary.[13] The work of adhesion of the LC to the support is given by the expression

$$W_a(\theta) = \gamma_L(\theta) + \gamma_s - \gamma_{Ls}[\theta]$$

When there are dispersion forces between the LC and the support, the equation for the work of adhesion becomes:

$$W_a(\theta) = 2[\gamma_L(\theta)\gamma_s]^{1/2}$$

From this it follows that

$$\gamma_{Ls}(\theta) = \gamma_s + \gamma_L(\theta) - 2[\gamma_L(\theta)\gamma_s]^{1/2}$$

Assuming that the LC orientation produced corresponds to a minimum interfacial surface energy $\gamma_{Ls}$ gives:

$$\frac{\partial\gamma_{Ls}(\theta)}{\partial\theta} = \frac{\partial\gamma_L(\theta)}{\partial\theta}\left[1 - \left(\frac{\gamma_s}{\gamma_L(\theta)}\right)^{1/2}\right] = 0$$

and the following typical cases[79] of homeotropic orientation on a support with $\gamma_S < \gamma_L(0)$, oblique on a support with

$$\gamma_L(0) < \gamma_s < \gamma_L(\pi/2)$$

and planar on a support with $\gamma_L(\pi/2) < \gamma_S$.

A systematic physicochemical interpretation of surface orientation has been proposed.[80] The values of the surface energy and the work of adhesion are written as the sum of dispersion and polar components:

$$\gamma_s = \gamma_s^d + \gamma_s^p$$
$$\gamma_L = \gamma_L^d + \gamma_L^p$$
$$W_a = W_a^d + W_a^p$$

where the indices $d$ and $p$ correspond to the dispersion and polar components of the interaction. $W_a$ can be represented as:[81]

$$W_a^d = 2\,[\gamma_s^d \gamma_L^d(\theta)]^{1/2}$$

The total interfacial surface energy is then written as:[80]

$$\gamma_{Ls}(\theta) = \{(\gamma_s^d)^{1/2} - [\gamma_L^d(\theta)]^{1/2}\}^2 + \{(\gamma_s^p)^{1/2} - [\gamma_L^p(\theta)]^{1/2}\}^2$$

For the dispersion part of the surface tension it is possible to write[72]

$$\gamma_L^d(\theta) = (\gamma_L^d)_0 + \Delta\gamma_L^d \sin^2\theta$$

and for the polar part:[33]

$$\gamma_L^p(\theta) = (\gamma_L^p)_0 + \Delta\gamma_L^p \sin^2(\theta - \theta_p)$$

where the angle $\theta_p$ is introduced to take account of the spontaneous polarisation of the surface layer. If the characteristics of the support $\gamma_s^d$ and $\gamma_s^p$ and the characteristics of the LC $(\gamma_L^d)_0$, $\Delta\gamma_L^d$, $(\gamma_L^p)_0$, $\Delta\gamma_L^p$, and $\theta_p$ are known, the condition for a minimum $\theta_{Ls}(\theta)$ can be used to calculate the value of the angle $\theta$ between the director and the normal to the support. This method was used[80] to construct a diagram showing the orienting influence of supports of different kinds (Fig.11).

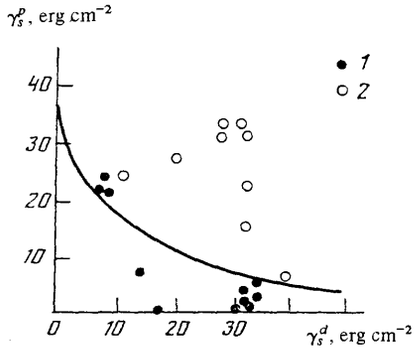



**Figure 11.** Diagram for determining the orientation of MBBA on supports (below the continuous theoretical curve, normal orientation of MBBA is assumed). The experimental points correspond to the known values of $\gamma_s^p$ and $\gamma_s^d$ for different supports; *1*) observed homeotropic orientation, *2*) oblique or planar.[80]

The polar and dispersion contributions to the surface energy have been determined[82] for two types of LC and supports treated with Chromolan solutions of different concentration. The polar $\gamma_s^p$ and dispersion $\gamma_s^d$ contributions to the surface energy of the supports were calculated by the least-squares method using the equation

$$1 + \cos\alpha = 2\,[(\gamma_s^d \gamma_L^d)^{1/2} + (\gamma_s^p \gamma_L^p)^{1/2}]/\gamma_L \qquad (18)$$

where $\alpha$ is the experimentally determined contact angle of wetting of the surface being studied by an isotropic liquid with known values of the polar $\gamma_L^p$ and dispersion $\gamma_L^d$ contributions to $\gamma_L$. The contact angles of wetting of these supports by the liquid-crystal material were then measured, and Eqn.(18) was used to determine $\gamma_L^p$ and $\gamma_L^d$ for the liquid crystal. Decrease in both the polar and the dispersion components of $\gamma_S$ facilitates the homeotropic orientation of the LC.

## VIII. INFLUENCE OF THE AZIMUTHAL ANISOTROPY OF THE SUPPORT ON SURFACE PHENOMENA

The characteristic features of the orientation of specific LC between two treated plates, and different methods of depositing coatings, have been described in detail.[29,36,37] The question of the extent to which the relief of the treated support and its anisotropy influence the orientation of the director and the contact angles of liquid-crystal droplets can be considered.

Rubbing a support always produces an axis of easy orientation in the plane of the support. This can be explained from purely geometric considerations.[1,47] Rubbed polymer films such as polyvinyl alcohol (PVA), polyamides, polyesters, polysiloxanes, etc. produce uniform ordering with a very small angle of inclination of the director to the plane of the support.[83] Rubbing glass with diamond paste produces well-formed grooves, along which the rod-shaped NLC molecules are arranged. Rubbing polymer coatings leads to local fusion of the polymers and orientation of the polymer chains along the direction of rubbing. Rubbing a glass plate with paper produces regions with a high temperature, leading to local fusion of the cellulose and subsequent orientation of the polymeric cellulose molecules along the direction of rubbing. Thus the orientation of NLC molecules is determined by the combined effect of the geometric (steric) factor and the anisotropic dispersion interaction between the oriented polymer and the NLC molecules.[83]

Coatings of pure metals, for example Al and Au,[84] facilitate planar orientation of LC. Depositing $SiO_2$ or metals on supports at different angles gives different angles of inclination of the director to the support.[10,36,83–88]

Experiments to determine the influence of the anisotropy of a support on the orientation of NLC have been carried out using the SAS hexadecyltrimethylammonium bromide (STAB).[20,89] The STAB molecules were adsorbed on the glass surface from solutions with different concentrations, so that monomolecular layers with different (parallel or perpendicular) orientations of the long axes of the STAB molecules were produced. In the first case, MBBA molecules are also oriented parallel to the surface of the support and the direction in which the plate was withdrawn from the STAB solution. In the second case, the homeotropic MBBA texture was produced. The role of rubbing in this experiment is played by the flow of the STAB solution along the glass plate, creating the required anisotropy of the support. Plates covered with STAB were used to measure the flow angles $\alpha_f$ and the wetting angles (established) $\alpha$ of droplets of nematic and isotropic MBBA at different temperatures (Fig.12). No break was observed for the angles $\alpha_f$ and $\alpha$ at the phase transformation from the nematic to the isotropic phase if the MBBA was oriented homeotropically on the support. On a support producing planar orientation, only the angle $\alpha_f$ changed smoothly, and on going to the nematic temperature range the NLC wet the support completely ($\alpha = 0$). The experimentally determined $\gamma_L(T)$ relationship did not show any unique features close to $T_c$. The measured values of the angles $\alpha$ were used to calculate the work of adhesion. The observations described above show that the orientation of the SAS molecules on the support has a significant influence on the orientation of NLC molecules.

Thus SAS which bring about the homeotropic orientation of NLC have their long molecular axes arranged at right angles to the surface, and the molecules of SAS which bring about planar orientation of NLC are usually arranged parallel to the surface of the support.[36,90,91] Two examples of the orientation of SAS on a support are shown in Fig. 13.

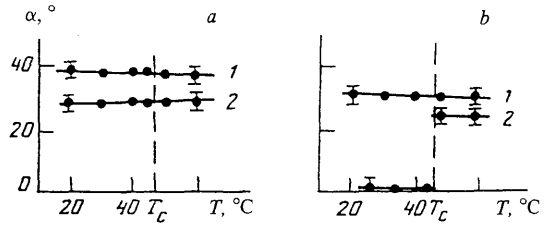



**Figure 12.** Temperature dependence of the angles of flow $\alpha_f$ (*1*) and the contact angles of wetting $\alpha$ (*2*) of drops of MBBA in the nematic and isotropic phases with homeotropic (*a*) and planar (*b*) orientation on STAB supports.[20]

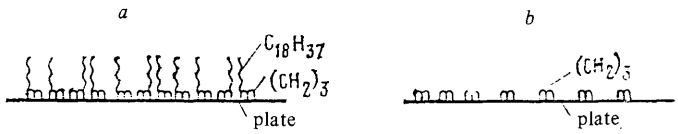



**Figure 13.** Diagram showing the arrangement of the molecules of the alkoxysilanes DMOAP (*a*) and MAP (*b*) on the surface of a support.[90]

Both thermodynamic considerations (minimisation of the inter-phase surface energy) and the steric factor (that is the surface relief) are used to explain the homeotropic texture. The orienting influence of the amphiphilic films studied[92,93] decreases with increase in the density of packing of the molecules. The contact wetting angles $\alpha$ decrease with increase in the area $A$ corresponding to one molecule of the SAS layer (Fig. 14). At the same time the contact angles are independent of temperature in the range 25–50 °C when the angle is measured to within ±1°. The work of adhesion $W_a$ increases smoothly with increase in $A$. These results were explained by the steric mechanism of orientation,[93] where the long NLC molecules are arranged in the depressions between the molecules of the amphiphilic monolayer, adopting the corresponding orientation, which is then propagated into the bulk of the NLC.

On anisotropic supports, the contact angles of wetting should depend on the azimuthal orientation of the cross-section of the drop, that is the measured angles $\alpha$ depend on the angle $\phi$ measured from the direction distinguished on the support. The anisotropy of the critical surface tension $\gamma_c$ on a support with a deposited layer of $SiO_2$ for two mutually perpendicular directions on the support has been described. The value of $\gamma_c(\phi)$ was determined by Zisman's method, by measuring the contact angles of a series of organic liquids: the values obtained were $\gamma_c(0) \cong 37$ erg cm$^{-2}$, $\gamma_c(\pi/2) \cong 39$ erg cm$^{-2}$.[94]

The wetting angles of liquid-crystal drops on supports whose anisotropy was produced by rubbing have been measured.[95] It was assumed that the interaction of the LC with the support involves dispersion forces (index $d$) and hydrogen bonding (index $h$), so that the surface tension at the LC–support boundary is written as

$$\gamma_{Ls} = \gamma_s + \gamma_L - 2(\gamma_s^d \gamma_L^d)^{1/2} - 2(\gamma_s^h \gamma_L^h)^{1/2} \qquad (19)$$

and the wetting angle is given by the expression

$$1 + \cos\alpha = 2[(\gamma_L^d \gamma_s^d)^{1/2} + (\gamma_L^h \gamma_s^h)^{1/2}]/(\gamma_L^d + \gamma_L^h) \qquad (20)$$

in which all the parameters depend on the azimuthal orientation of the cross-section of the drop. The wetting angles of an ethanol–water mixture with known values of $\gamma_L^d$ and $\gamma_L^h$ were first measured, and used to determine the parameters $\gamma_s^d$ and $\gamma_s^h$ for different supports; these parameters and the measured wetting angles of nematic 7CB were then used to calculate the surface tension of the latter.[95]

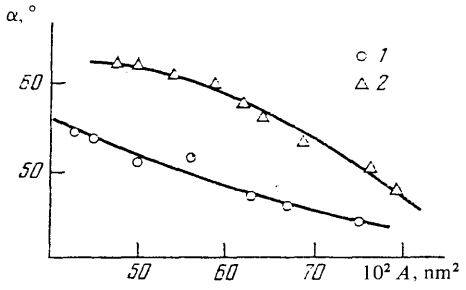



**Figure 14.** Dependence of the wetting angles $\alpha$ of drops of MBBA on supports covered with a layer of *DL*-γ-palmitoylisolecithin (*1*) and *DL*-β,γ-dilauroyl-α-lecithin (*2*) on the area $A$ at 35 °C.[92]

The contact angles were measured in two vertical cross-sections of the drop: one section was parallel to the orientation of the director on glass with a deposited layer of $SiO_2$ ($\alpha_\parallel$), and the other perpendicular to the axis of easy orientation ($\alpha_\perp$). The corresponding values of $\gamma_{s_\parallel}$, $\gamma_{s_\perp}$, $\gamma_{L_\parallel}$, and $\gamma_{L_\perp}$ were calculated using Eqns. (19) and (20).

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Thus available experimental data on the surface tension of the nematic and isotropic phases of nematogenic compounds are often contradictory, and are clearly inadequate for developing a general model of the surface tension of liquid-crystal compounds. Existing theories have proved to be applicable only for individual substances (Okano and Murakami,[25] Gannon and Faber[8]), or to explain experimental phenomena at a qualitative level (Parsons,[30] Croxton[34]).

The anchoring of liquid crystals to a support has been studied in more detail, undoubtedly because of the interest in the practical applications of liquid crystals. The surface energy of adhesion is introduced in a form convenient for calculation, and makes possible a satisfactory description of the experimental results, but the physical nature of the energy of adhesion has not yet been sufficiently fully studied.

Studies of texture transformations induced by a surface have been published comparatively recently, and are predominantly theoretical. In spite of some contradictions, a number of serious experimental studies have proved the existence of a nematic order parameter induced by the support in the isotropic phase of an LC. The theoretical interpretation of these phenomena, however, is restricted to the Landau–de Gennes phenomenological explanation.

The experimental temperature dependence of the angle of inclination of the director to the free surface gives sufficient material for the development of a theoretical model. Neither the simplest thermodynamic considerations (Faetti and Fronzoni[9]), nor the extensive assumptions of the calculation of the moments of the forces on the surface (Mada[73,74]) are satisfactory, however.

The calculation of the dispersion and polar components of the surface energy, and attempts to introduce the orientation of the director into the calculations, are necessary steps in the development of theories of the mechanism of the orientation of LC. Nevertheless, up to the present these calculations have been based on phenomenological arguments and have not been related to models of the anisotropic interaction potential.

Practical requirements (the production of displays, radiant energy indicators, etc.) are making it necessary for research workers to learn to predict the characteristics of developed liquid-crystal elements. The large number of studies describing practical methods for producing stable LC textures show clearly the variety of orienting factors, including physicochemical interaction and the three-dimensional structure of the support and the oriented LC layer. The attempts which have been made, however, to formulate the conditions which would make it possible to predict the orientation of the director from the physicochemical characteristics of a liquid crystal and a support have not yet led to the development of criteria suitable for all LC–support pairs studied. Success will probably be achieved by a combined study of the physicochemical parameters of the surface of the support, the surface of the liquid crystal, and various phenomena associated with the interaction of the LC with the support.

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# Stereochemical Aspects of the Dimerisation of Phosphazo-compounds

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The review considers the influence of the electronic and steric structures of phosphazo-compounds on the position of their monomer-dimer equilibrium in solution. It is shown that, for acyclic phosphazo-compounds, the decisive factors are, together with steric factors, the apicophilicity of the substituents at the phosphorus atom and the donor-acceptor properties of the substituents at the nitrogen atom of the phosphazo-group. The shift of the equilibrium towards the dimers observed for phosphazo-compounds with strained five-membered phosphorus-containing heterocycles can be accounted for by the increased apicophilicity of the endocyclic substituents at the phosphorus atom. Other characteristic features of the dimerisation of cyclic phosphazo-compounds are also discussed.
The bibliography includes 62 references.

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## I. INTRODUCTION

The first monomeric phosphazo-compounds (PAC) $R'_3P{=}NR$, where R = alkyl, aryl, or ArCO and R' = alkyl or aryl, were synthesised in 1919.[1] The dimeric PAC $(PhN = PCl_3)_2$ had been described even earlier.[2] However, serious studies on the physical and chemical properties of compounds of this kind and especially on the relation between their monomeric and dimeric forms did not begin until 1959 when Zhmurova and Kirsanov obtained a whole series of trichlorophosphazo-arenes (TCPA-arenes) and showed that they are almost all dimeric under normal conditions.[3] In the subsequent studies[4-10] it was shown that dimerisation is a specific feature of trichloro- and certain phenyldichloro-phosphazo-hydrocarbons.

The mechanism of the reaction leading to the formation of dimers was discussed by Zhmurova and Kirsanov[11] in relation to the interaction of phosphorus pentachloride with aromatic amines in benzene:

$$PCl_5 + 2ArNH_2 \rightarrow ArNHPCl_4 + ArNHCl$$

$$\underset{1}{\downarrow} \qquad \underset{2}{\downarrow}$$

$$HCl + {}^1/_2\,(ArNPCl_3)_2 \xrightarrow{\text{refluxing}} ArNPCl_3 + HCl.$$

The study of the infrared spectra of the reaction mixture at room temperature demonstrated the presence of an absorption in the range 3310–3320 $cm^{-1}$, which is characteristic of the N–H bond. From this, the authors assumed that the existence in solution of the unstable intermediate arylamino-tetrachlorophosphoranes $ArNHPCl_4$ had been demonstrated; on heating and also *in vacuo* at room temperature, these substances split off hydrogen chloride and are immediately converted into the dimeric TCPA-arenes (pathway *1*). The cryoscopic determination of the molecular weights of the TCPA-arenes obtained (when these are sufficiently soluble in benzene) yields values corresponding to twice the molecular weights of the monomeric forms.[3] Pathway *2* is rejected owing to the lack of absorption in the range at 1320–1380 $cm^{-1}$, attributed to the P=N bond. This absorption, indicating the presence of monomeric TCPA-arenes, appears only after refluxing a benzene solution.

On the other hand, in a later study[12] it is claimed that the reaction considered leads to the monomeric compounds $ArNPCl_3$, which are in many cases capable of dimerising. The existence of arylaminotetrachlorophosphoranes was not confirmed. The $^{31}P$ NMR spectra obtained by the authors for the reaction mixture in different solvents (including benzene) demonstrated the presence of monomeric forms, characterised by signals in the vicinity of −50 p.p.m. In certain cases yet another higher-field signal in the region of −80 p.p.m. was present in the spectrum. The relative rarity of this signal, which is due to the dimeric product $(ArNPCl_3)_2$ readily isolated on evaporating the solution, is usually caused by the inadequate solubility of the dimer and not by its absence from the reaction mixture.

The existence of dynamic equilibrium between the monomeric and dimeric forms of the TCPA-compounds in solution has also been confirmed by a study[13] of the dependence of this equilibrium on various factors. It was noted that an increase of temperature increases the fraction of the monomer in solution. The influence of the solvent is frequently decisive, although it has still not been explained. Despite the large number of experiments and the wide variety of the solvents employed, no direct relation has been found between the dielectric constants or dipole moments of the solvents and the monomer : dimer ratio. The dependence of this ratio on the solution concentration also remains unexplained.

The principal empirical criteria determining the conditions for the existence of the dimeric PAC as a function of the type of substituents at the phosphorus and nitrogen atoms of the phosphazo-group (the PA-group) were first formulated by Zhmurova and Kirsanov,[3] who established that the observed dimers are characterised by the presence at the phosphorus atom of three strong acceptors—fluorine or chlorine atoms. The replacement of even one of these by a more electron-donating group, for example, the phenyl group, leads to the complete or partial conversion into the monomeric form. Alkoxy- and aryloxy-dihalogenophosphazo-arenes were found to exist only in the monomeric form and this also applies to the PA-acyl derivatives. Hydrocarbon residues, unbranched alkyl or aryl groups, must be present

at the nitrogen atom in the dimeric PAC. Steric factors play a major role in the dimerisation process. An increase in the bulk of the substituents both at the phosphorus and nitrogen atoms hinders dimerisation, displacing the equilibrium towards the monomeric form.

The greater or lesser tendency of the TCPA-arenes towards dimerisation depends to a large extent on the basicity of the initial anilines.[3-12] Trichlorophosphazoarenes derived from anilines with $pK_a \leq 0$ exist only as monomers. The presence in solution of an equilibrium mixture of the monomeric and dimeric species is characteristic of derivatives of anilines with $pK_a \cong 0-2$. Only dimeric PAC have been obtained from anilines with $pK_a > 4$.

Unfortunately empirical rules of this kind hold only for a limited series of compounds. In the present review attention is concentrated on a more general theoretical approach which makes it possible to relate clearly the state of the monomer–dimer equilibrium to the electronic and steric structures of a wide variety of PAC (including cyclic compounds).

## II. GEOMETRICAL STRUCTURE AND CERTAIN PHYSICOCHEMICAL PROPERTIES OF PHOSPHAZO-COMPOUNDS

Monomeric PA-hydrocarbons are reactive low-melting crystalline substances or liquids, which readily dissolve in non-polar organic solvents. With increase of temperature, the $^{31}P$ NMR signal undergoes an appreciable upfield shift.[13] The geometrical parameters of a series of structurally investigated monomeric PAC have been published.[14] The correlation, found previously,[15] between the length of the P=N double bond and the valence angle at the nitrogen atom was noted. With increase of this angle, the P=N bond is shortened owing to the improvement of the conditions for the overlap of the orbital of the lone electron pair (LEP) of the nitrogen atom and the phosphorus orbital and the decrease of the covalent radius of the nitrogen atom. A typical feature of monomeric PAC in the crystal is their preferential existence in the uneclipsed conformation, as shown in Fig. 1*a* for $Ph_2PF{=}NMe$.[16] The eclipsed conformation has been observed only for $Cl_3P{=}NCCl(CCl_3)_2$.[14]

The barrier to rotation about the P=N double bond is unusually low. The paper quoted by Romanenko and Povolotskii[17] indicates values in the range 8.8–29.7 kJ mol$^{-1}$, i.e. of the same order of magnitude as the barriers to rotation about single P=N bonds, which ensures the stability of rotation (albeit hindered) about the P=N bond.

In contrast to the monomeric PAC, their dimeric analogues melt at fairly high temperatures and are much less soluble.[18] Many chemical reactions involving dimeric PA-hydrocarbons are much slower than those of the monomers or do not occur at all. The shielding of the phosphorus nuclei in the dimers is almost independent of temperature.[13]

The energy of the PN bond in the $(MeNPCl_3)_2$ dimer proved to be 311.1 kJ mol$^{-1}$,[4,5] which is appreciably higher than the 279.7 kJ mol$^{-1}$ characteristic of $P(NEt_2)_3$ and is close to the values of 302.7 and 303.6 kJ mol$^{-1}$ corresponding to the trimeric and tetrameric cyclophosphazenes. From this, Zhmurova and Kirsanov[3] proposed a cyclic structure for dimeric PA-hydrocarbons with four equalised endocyclic PN bonds, characterised by a considerable proportion of double bond character, as the most probable. X-Ray diffraction studies on the dimeric structures in the crystalline state[19-23] made it possible to refine this picture. As an example, Fig. 1*b* presents the molecular structure of the dimer $(Ph_2.PFNMe)_2$.[23]

In the dimeric PAC the configuration of both phosphorus atoms approaches the trigonal bipyramidal configuration with the F atoms at the apices of the pyramid. On the grounds that the equatorial P=N bonds are appreciably shorter than the single P–N bond in $[H_3^+NPO_3^{2-}]Na^+$, whose length is 1.77 Å,[24] it was concluded that the LEP of the nitrogen atoms in these bonds are delocalised.[25] A correlation has been noted[23] between the increase in the length of the P–N bonds and the decrease of the electronegativity (EO) of the ligand R in the series $(RPF_2NMe)_2$, where R = F, $CCl_3$, $C_6F_5$, or Ph. The spin–spin coupling constant $^2J_{PP}$ is also determined by the EO of the residue R: 125 Hz for $CCl_3$, 111 Hz for $C_6F_5$, and 80 Hz for Ph. The lowest value $^2J_{PP}$ = 28 Hz, found for $(Ph_2PFNMe)_2$, can be explained by the effect of the replacement of F by Ph at the phosphorus atom. A satisfactory correlation is observed between the intramolecular P...P distance $l$ and the constant $^2J_{PP}$ in the series $(R^1R^2PFNMe)_2$; $l$ = 2.579 Å for $R^1$ = F and $R^2$ = $CCl_3$, $l$ = 1.594 Å for $R^1$ = F and $R^2$ = $C_6H_5$, $l$ = 2.61 Å for $R^1$ = F and $R^2$ = Ph, and $l$ = 2.659 Å for $R^1 = R^2$ = Ph.

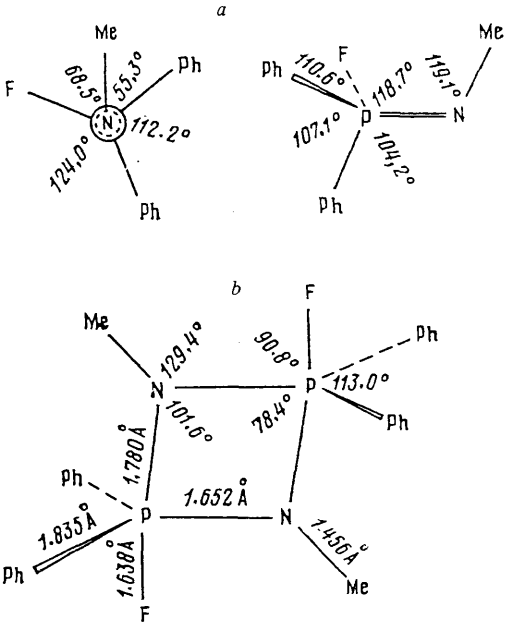
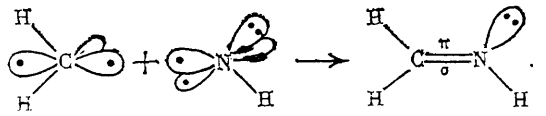



Figure 1. The molecular structures of $(Ph_2PFNMe)_n$: *a*) monomer ($n$ = 1);[16] *b*) dimer ($n$ = 2).[23]

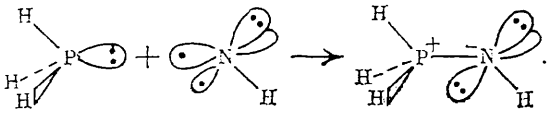
## III. ELECTRONIC STRUCTURE OF PHOSPHAZO-COMPOUNDS

A discussion of the nature of the P=N bond in phosphazines may be found, for example, in Allcock's monograph,[26] where numerous references to the relevant communications are given. In considering the characteristic features of the P=N double bond, which determines the reactivity of the PA group, it is sufficient to compare in terms of the same $s$, $p$ valence orbitals the formally analogous P=N and C=N bonds in the model compounds $H_3P{=}NH$ and $H_2C{=}NH$ respectively.

The localised molecular orbitals (LMO) of the σ and π types can be readily constructed for the C=N bond in the azomethine from the valence orbitals of the C and N atoms:

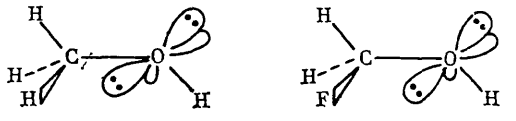


The polarity of the bond is determined by the difference between the EO of carbon and nitrogen. An analogous covalent structure of the P=N bond is impossible owing to the deficiency of the atomic orbitals (AO) of phosphorus. The formation of $H_3P{=}NH$ can be represented as a result of the σ-dative interaction of the phosphorus LEP in the phosphine ($H_3P$) molecule with the valence $sp^2$-hybridised nitrogen AO of the NH directed towards it:



The disposition of all three electrons in the LMO corresponding to the constituent of the P–N bond is unfavourable, since one of them must be located in the high-energy antibonding σ* LMO. The migration of this electron to another valence AO of nitrogen with formation of a new LEP of the π type is more probable. The PN bond is then found to be highly polarised, much more than would follow from the EO of the P and N atoms. The reverse transfer of electron density from the nitrogen atom to the $H_3P$ group via a hyperconjugation mechanism leads to some redistribution of such electron density from the LEP of nitrogen mainly over the H atoms. Thus, in contrast to the C=N bond, the formally double P=N bond is characterised by a dominant contribution of the $P^+{-}N^-$ structure, which ensures a relatively low barrier to rotation about this bond and the high reactivity of the atoms of the PA group. The use of the 3*d* AO of phosphorus which are unoccupied in the ground state leads to some decrease of the excess positive charge on phosphorus owing to its $p_\pi{-}d_\pi$ bonding to the nitrogen atom. However, this compensation cannot be effective because of the much higher energy level of the 3*d* AO compared with other (valence) phosphorus orbitals.

The analogous structures of methanol ($H_3C{-}OH$) and its substituted derivatives, which have been thoroughly investigated, may be adopted as models of the electronic and steric structures of the monomeric PAC:[27]



(I) (II)

As for $H_3P{=}NH$,[28] the uneclipsed conformation of methanol (I) is the most stable, which can be accounted for by the destabilising effect of the repulsion of the occupied σ constituents of the LMO corresponding to the CH and OH bonds. The replacement of one of the H atoms attached to carbon by an electronegative substituent such as F leads to the preferential *gauche*-conformation (II) stabilised by the interaction of the $p_\pi$ LEP of the oxygen atom with a vacant σ* LMO of the C–F bond. The other oxygen LEP has an appreciable *s* character and cannot participate quite so actively in π bonding to the $CH_2F$ group. As we have seen, a similar situation is observed for $Ph_2PF{=}NMe$.

The electronic structure of dimeric PAC can also be modelled using *s*, *p* valence orbitals. The apical substituents in the trigonal bipyramid (TBP) of phosphorus are distinguished by longer (and weaker) bonds with the central atom compared with the equatorial bonds. Both σ bonds at the phosphorus atom of this type can be described in terms of the three MO of a single three-centre four-electron bond in which only one of the 3*p* AO of phosphorus is involved and is directed along the axis. With increase of the EO of the apical substituents, the stability of such a system also increases.[29] The more electron-donating substituents therefore prefer equatorial positions in the TBP. The presence of the LEP at the bonding atom of such a substituent is responsible for its destabilising interaction with the occupied σ MO of the axial bonds as a result of which the LEP is located in the equatorial plane. Conversely, the presence of an unoccupied orbital in the bonding atom of the substituent increases its chance of occupying an apical position.

The greater or smaller ability of two different substituents to occupy apical positions in the TBP of phosphorus is characterised by their relative apicophilicities. The latter can be estimated from the energy change when the above substituents are exchanged between the apical and equatorial positions. Series of substituents in terms of decreasing apicophilicities have now been established, for example:[29]

$$F{>}H{>}Cl{\sim}C(O)R{>}Br{\sim}CN{>}OPh{\sim}SPh{>}OR{>}NR_2{>}Me{>}Ph.$$

These are only approximate and, as we shall see below, may break down under certain conditions. Nevertheless, in discussing the stability of any TBP, be it the transition state in the nucleophilic substitution reaction at a tetracoordinate phosphorus atom or a stable phosphorane structure, the concept of the apicophilicity of the substituent is much more convenient than, for example, the concept of its EO.

## IV. THE MECHANISM OF DIMERISATION

The observed tendency of PAC towards cyclodimerisation is due to the enhanced electrophilicity of the positively charged phosphorus atom and the enhanced nucleophilicity of the negatively charged atom in the PA group. In principle, two mechanisms are possible for the dimerisation of the PAC $XY_2P{=}NR$—stepwise and synchronous. The former can be formulated on the basis of the existence of the monomers in the most stable (uneclipsed) conformation (Fig.2). The reaction begins with the attack by the $N^1$ atom of one of the monomers via its LEP on the $P^2$ phosphorus atom of another monomer molecule from the side opposite to the direction of the bond between $P^2$ and the most apicophilic of its substituents ($X^2$). The formation of the new bond leads to the transition of the $P^2$ atom from the tetrahedral to the TBP configuration and is accompanied by the transfer of one electron from the first monomer to the second. The tendency of the π-LEP of the negatively charged $N^2$ atom to be located in the equatorial plane of the TBP promotes the rotation of the $N^2{-}R^2$ group about the $P^2{-}N^2$ bond, which places the $sp^2$-hybridised LEP of $N^2$ in the position most favourable for the formation of a dative σ-bond with the positively charged $P^1$ atom. The rotation of the $P^1X^1Y_2^1$ group about the $N^1{-}P^1$ bond is also essential for the closure of the four-membered diazadiphosphetidine ring.

However, it is entirely possible that the barriers to rotation about the $P^2{-}N^2$ and $N^1{-}P^1$ bonds are relatively large and the energy of the $P^2{-}X^2$ axial bond is fairly small. In this case the attack by $N^1$ on $P^2$ can terminate via the mechanism of the usual nucleophilic $S_N2$ substitution: by the elimination of the

apical substituent $X^2$ in the form of an anion and the formation of a more or less stable linear cation $[X^1Y^1_2P^1{-}N^1(R^1){-}P^2(Y^2_2){=}N^2R^2]^+$.

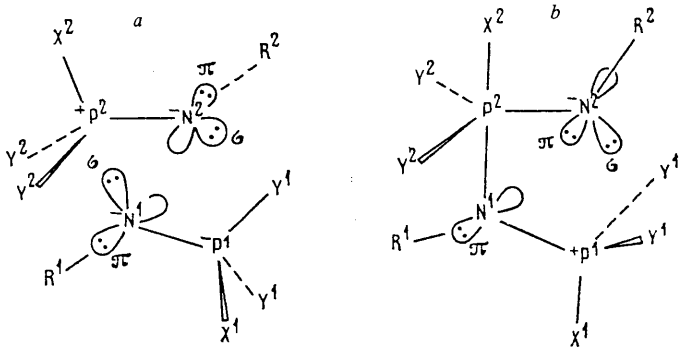


Figure 2. The mechanism of the stepwise dimerisation of phosphazo-compounds: *a*) disposition of the monomers in the formation of the first "dimeric" NP bond; *b*) conformation of the intermediate linear dimer most suitable for ring closure.

For the second mechanism to operate (synchronous dimerisation), the rotation about the $N^1{=}P^1$ and $N^2{=}P^2$ bonds in the monomers must take place beforehand, i.e. the monomers must be in the eclipsed conformation with a *cis*-disposition of the N–P and P–X bonds, which is energetically unfavourable but is more favourable for dimerisation. After this, both pairs of atoms ($N^1$, $P^2$ and $P^1$, $N^2$) can form the corresponding dative σ-bonds simultaneously. The problem of the possible preference for one of the dimerisation mechanisms discussed has not as yet been finally solved. It is also possible that everything depends on the reaction conditions: the presence of a specific solvent, the relative initial positions of the monomers, etc. Even the P=N–R valence angle apparently affects the dimerisation mechanism.[28] In the subsequent exposition we shall therefore confine ourselves to the synchronous reaction mechanism, since it is simpler.

## V. THE INFLUENCE OF THE ELECTRONIC AND STERIC STRUCTURES OF ACYCLIC PHOSPHAZO-COMPOUNDS ON THE POSITION OF THEIR MONOMER–DIMER EQUILIBRIUM

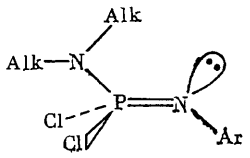
We shall now consider in greater detail the factors which determine the greater or smaller tendency of PAC to dimerise. They can be arbitrarily divided into two groups—electronic and steric. The former include those which influence the electrophilicity of the phosphorus atom and (or) the nucleophilicity of the nitrogen atom of the PA group and also ensure the stability of the trigonal bipyramidal configuration of the P atoms in the dimers. The most important of these factors is the apicophilicity of the substituents at the phosphorus atom already considered.

Despite the fact that in the nucleophilic attack on the phosphorus atom only one of its three substituents in the PA group enters an apical position in the TBP group formed, a high EO of the remaining substituents is also desirable for dimerisation. An increase in the EO of these substituents not only increases the relative contribution of the AO of phosphorus to the unoccupied MO of the monomer but also leads to a greater decrease of the energy levels of these MO compared with the occupied orbitals. Both these factors intensify the interaction between the monomers, which leads to their dimerisation.[28,30]

A similar effect is induced also by the enhancement of the electron-donating properties of the substituent R at the nitrogen atom, which leads to an increase of the negative charge on the nitrogen AO and to a greater rise of the energy levels of the occupied MO of the PA group compared with the levels of the unoccupied MO. The width of the energy gap between these MO diminishes and the interaction between the monomers is correspondingly intensified.[28]

Speaking of the steric factors influencing the dimerisation of PAC, one should note in the first place the steric factors already mentioned. The presence of hindrance interfering with the disposition of the monomers at a distance necessary for the onset of dimerisation or their most favourable orientation relative to one another shifts the monomer–dimer equilibrium towards the monomer. Many instances of precisely such influence of very bulky substituents in the PA group are available in the literature (see, for example, Kozlov et al.[31]).

Since the different conformations of the monomeric PAC are not equally favourable for dimerisation, the factors stabilising one of them can play an appreciable and sometimes even a decisive role in the equilibrium considered. As an example, one may quote the effect of the replacement of one of the chlorine atoms in TCPA-arenes by the dimethylamino-group. The atomic EO of nitrogen and chlorine on Pauling's scale are approximately the same. In contrast to chlorine, the $NAlk_2$ group with an $sp^2$-hybridised nitrogen atom has a plane of symmetry and not an axis of symmetry, which is not only responsible for the presence of a barrier to rotation about the P–N single bond but also influences the barrier to rotation about the P=N double bond. The conformation (III) is energetically most favourable.



(III)

Other possible conformations, obtained by rotation about the P=N bond, are characterised by an increase of the total energy of the molecule both as a result of the breakdown of the conjugation of the LEP of the nitrogen atom in the dialkylamino-group with the rest of the molecule and as a consequence of the increasing repulsion between this LEP and the $sp^2$-hybridised LEP of the imino-nitrogen atom. Thus the presence of the dialkylamino-group as a substituent at the phosphorus atom of the PA group stabilises the conformation unfavourable for dimerisation. Ultimately the tendency of the PAC to dimerise diminishes.[18]

Cases where the difference between the monomer–dimer equilibrium positions can be explained by a change in only one factor are very rare. Usually several different factors change simultaneously and in the explanation of the observed shift of the equilibrium it is essential to take into account the effects of each. As an example of the situation where the replacement of only one substituent leads to an extremely marked shift of the equilibrium, induced by the superposition of several effects acting in one direction, it is sufficient to compare the capacities for dimerisation of PA-arenes and PA-acyl derivatives

The triphenylphosphazoacyl derivative $Ph_3P{=}N{-}C(O)Ph$ investigated by Bar and Bernstein[32] is characterised by the eclipsed conformation typical for PAC with an almost planar disposition of the P=N–C=O fragment (Fig. 3*a*). The appreciable contribution of the limiting structure illustrates in Fig. 3*b* the increase of the stability of this conformation. The formation of a weak non-valence bond between the charged $P^+$ and $O^-$ atoms entails a change in which the tetrahedral configuration of the phosphorus atom approaches the trigonal bipyramidal configuration. Despite the corresponding decrease of the P=N bond order, the barrier to rotation about this bond should increase.

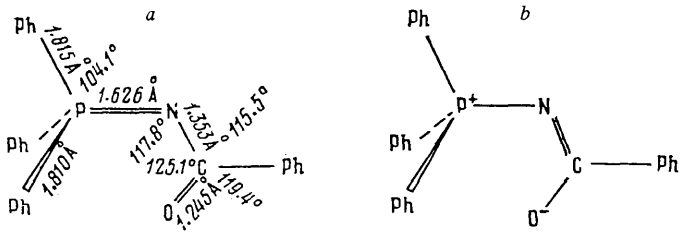
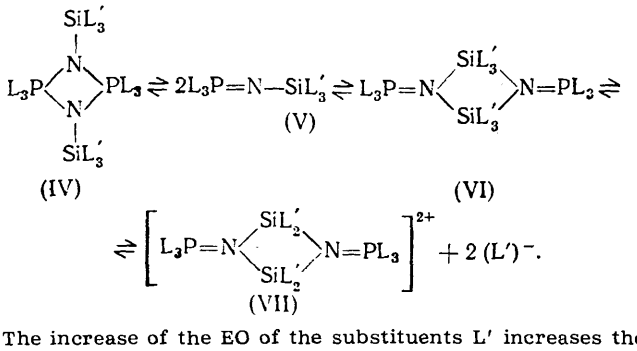



Figure 3. The molecular structure of $Ph_3P{=}N{-}C(O)Ph$: *a*) principal geometrical parameters; *b*) the limiting structure whose contribution increases the stability of the monomeric form [32]

The electrophilicity of the phosphorus atom diminishes on passing to the TBP configuration. As a consequence of the migration of the negative charge from phosphorus to oxygen and not nitrogen, the latter also becomes less nucleophilic. All these factors explain why, in contrast to PA-arenes, the PA-acyl derivatives do not dimerise under any conditions.

In conclusion of this Section, we shall consider the dimerisation of *N*-silyl-substituted PAC $L_3P{=}NSiL'_3$, described by Wolfsberger,[33,34] whose course is extremely unusual. When L′ = alkyl, they become like the usual PAC as regards dimerisation—the tendency to dimerise increases with increasing EO of the substituents L and the dimers themselves are diazadiphosphetidine rings with pentacoordinate phosphorus atoms:




The increase of the EO of the substituents L′ increases the positive charge on the Si atom, promoting an increase of its coordination and saturation. For this reason, in the presence of electron-donating substituents at the phosphorus atom (for example, L = alkyl) and of electron-accepting substituents at Si (for example, L′ = halogen), the Si atom may be more electrophilic than the phosphorus atom of the PA group. In this case the dimerisation takes place with formation of the four-membered ring $(NSi)_2$ with pentacoordinate Si atoms, as has been observed for L′ = F [structure (VI)]. In the pure state such substances are dimeric at room temperature. They are monomeric in solution, but, with decrease of temperature, they dimerise. The pentacoordinate nature of the silicon atom ensures a higher Si–F bonding energy. When the F atoms at the silicon atom are replaced by other halogens, the heterolytic elimination of the latter leads to the more stable dicationic structure (VII) in which the silicon atoms are tetracoordinate.

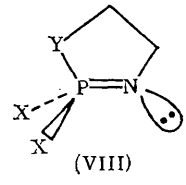
It is also noteworthy that, whereas the transition from the monomer (VI) to the dimeric structure (IV) is accompanied by the usual upfield shift of the $^{31}P$ NMR signal, the transition to structures (VI) and (VII) is characterised by downfield chemical shifts.

## VI. THE EFFECT OF THE FIVE-MEMBERED PHOSPHORUS-CONTAINING HETEROCYCLE

The chemistry of small (four- and five-membered) phosphorus-containing heterocycles has been developing vigorously in recent times. The characteristic features of their behaviour in chemical reactions have led to the differentiation of this group from other phosphorus compounds. The effect of the five-membered ring is manifested also in the monomer–dimer equilibrium considered here, shifting its position much further towards the dimer than is characteristic of, for example, acyclic PAC. The nature of this effect can be explained on the basis of the general ideas concerning the factors determining the tendency of PAC to dimerise described above.

### 1. Phosphazo-compounds with an Endocyclic P=N Bond

We shall consider initially 1,2-azaphospholes in which the P=N double bond is endocyclic:




(VIII)

Compared with acyclic PAC, these compounds have a whole series of characteristic features, which affect the reactivity of the PA group. Firstly, the presence of the almost planar five-membered ring is responsible for the unique eclipsed conformation (VIII) which is favourable for dimerisation. Secondly, the enhanced *p* character of the phosphorus atom in the P–Y and P=N bonds corresponds to a relatively small endocyclic Y–P=N angle (~90°), which is equivalent to a decrease of the EO of the phosphorus atom relative to its endocyclic substituents. The lengths of these bonds and the electron densities at the Y and N atoms increase. The *trans*-antiperiplanar disposition of the $sp^2$-hybridised LEP of the nitrogen atom relative to the P–Y bond causes an additional weakening of this bond as a consequence of the so-called stereoelectronic effect (see, for example, Gorenstein et al.[35] and the references therein).

The interaction of this LEP with the unoccupied σ* LMO of the P–Y bond reduces the overlap population between P and Y and its electrostatic (dipole) influence on the occupied σ LMO shifts the electron density from P to Y.[27] The changes

described are equivalent to an increase of the effective potential apicophilicity of the substituent Y and increase the probability of nucleophilic attack on the phosphorus atom along the P–Y bond on the opposite side.

Similar effects have been considered in detail in relation to the hydrolytic reactions of diethyl and ethylene phosphates.[35] The reaction profiles of the above reactions are compared in Fig. 4.[36]

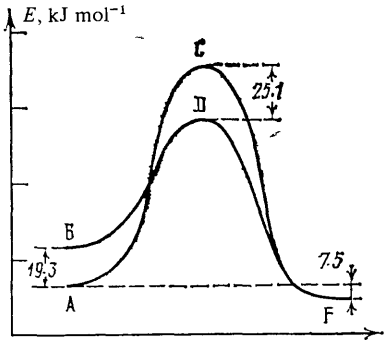
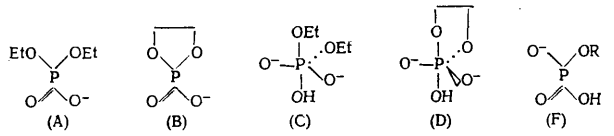


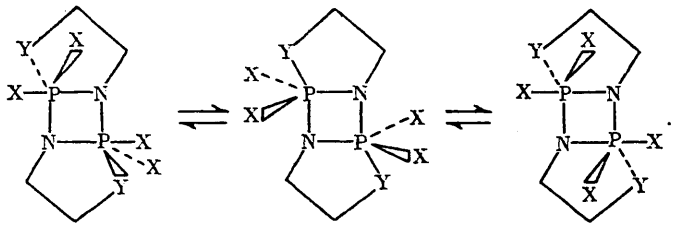

Figure 4. Reaction profiles of the hydrolytic reactions of diethyl phosphate (A) and ethylene phosphates (B) demonstrating the role of the five-membered ring in the energy relations of the transition from tetracoordinate to pentacoordinate phosphorus:[36]




Evidently the activation energy is much lower for the cyclic phosphate than for the acyclic phosphate. This difference is caused both by the angular strain in ethylene phosphate, which increases its energy by 19.3 kJ mol$^{-1}$ compared with diethyl phosphate, where the hybridisation of the tetracoordinate phosphorus atom is closer to equilibrium tetrahedral hybridisation, and by the stereoelectronic effect, which causes additional stabilisation of the apical-equatorial disposition of the five-membered ring in the trigonal bipyramidal transition state (25.1 kJ mol$^{-1}$).[35] The $p_\pi$ LEP of the endocyclic equatorial oxygen atom is orthogonal with respect to the three-centre axial O–P–O bond and the repulsion between the hybridised σ-LEP of this atom and the occupied O–P–O MO is weakened as a consequence of the *trans*-disposition of the corresponding dipoles.[27]

The energy balance in the dimerisation of PAC can be represented by two contributions of comparable magnitude with opposite signs: the energy expenditure on the transition of both phosphorus atoms from the tetrahedral to the TBP configuration and the energy gain on formation of two new P–N bonds.[37] It follows from the above that the energy expenditure on the rehybridisation of the phosphorus atom in the cyclic PAC is much smaller than in the acyclic compounds.

It has been noted[38] in relation to azaphospholes with Y = S or O that, on passing from the acyclic phosphorane to the phosphorane with a planar five-membered heterocycle, the length of the axial P–Y bond increases. Hence it follows that the "dimeric" P–N σ-bond, located approximately on the same axis as the P–Y bond, is stronger (and energetically more favourable), for example, in the tricyclic structure (IX) than in the analogous compound with opened five-membered rings.



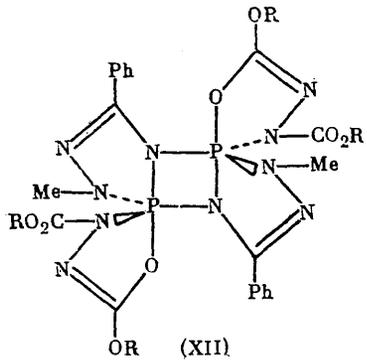

All this explains why the presence of the five-membered ring predetermines the enhanced tendency of 1,2λ$^5$-azaphospholes to add to the P=N bond and in particular their tendency to dimerise.[38–40] The electronic properties of the endocyclic substituent Y are then found to exert a decisive influence on the position of the monomer–dimer equilibrium.[41]

The structure of the dimer formed initially with a trigonal-bipyramidal coordination of the phosphorus atoms and the axial-equatorial dispositions of all three rings is characterised by the so-called meridional form (IX) in which all the bonds of the nitrogen atoms lie in the same plane.[42] The synchronous Berry pseudo-rotations[43] can convert the structure (IX) into any of the two facial forms (X) or (XI) with the nitrogen atoms in the pyramidal configuration. There is equilibrium between these forms in solutions, while in crystals one of them occurs (which particular one occurs depends on the relative apicophilicities of the substituents at the phosphorus atom). Experiments have shown that, for Y = O or S (and for the apicophilicity of X lower than that of Y), the form (IX) is observed,[38] while in the case where Y = N the position of the monomer–dimer equilibrium depends on the apicophilic properties of the exocyclic substituent X at the phosphorus atom. Dimeric forms of type (XI) are realised for 1,2,4,3λ$^5$-triazaphospholes, for example, with X = F, Cl, or Br, whereas in the case where X = OR, OAr, $NR_2$, or Ph only the monomeric forms obtain.[41] The absence of dimerisation for Y = C and apicophilic exocyclic substituents can be explained by the extremely high activation energy for the transition of phosphorus atoms from the tetrahedral to the TBP configuration with a diequatorial disposition of the five-membered ring.

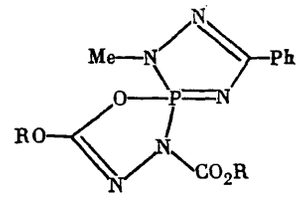
The dimeric form (X) has not as yet been observed in a pure form. Its presence as an admixture to the distorted form (IX) has been noted for dimeric 1,3,4,2λ$^5$-thiadiazaphospholes.[38] The distortion is caused by the angles at the phosphorus atom in the five- and four-membered ring being much smaller than 90°, which leads to the "fracture" of the TBP axis in the direction which is the opposite of that usually observed in acyclic phosphoranes. The decrease of the angle between the exocyclic equatorial substituents at the phosphorus atom to 110° corresponds to the "anti-Berry distortion" indicated.

In conclusion we shall consider the case where the exocyclic substituents at the phosphorus atom in 1,2-azaphospholes have been replaced by a second five-membered heterocycle. The synthesis of the four dimeric compound (XII),

where R = Me, Et, $CHMe_2$, and $CH_2Ph$, has been reported:[44]

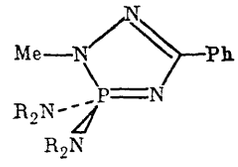


(XII)

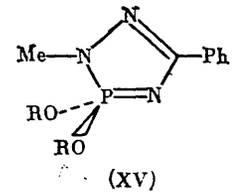


(XIII)

By hypothesis, they are formed as a result of the dimerisation of the spirocyclic intermediate (XIII). By comparing these unstable PAC with the similar monocyclic structures (XIV) and (XV), which exist in the monomeric form only,[41] we can see that the presence of the second five-membered heterocycle clearly enhances the tendency of the azophospholes to dimerise.



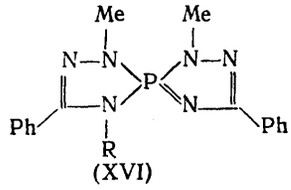
(XIV)



(XV)

The point is that the bicyclic structure (XIII) with a tetracoordinate phosphorus atom is subject to angular strain to a greater extent than the corresponding monocyclic structure. Although the oxadiazophosphole ring in the TBP of the dimer formed initially is in the diequatorial position, the synchronous Berry pseudorotations lead to the energetically more favourable structure (XII), where both five-membered heterocycles are located in the axial-equatorial positions and the most apicophilic substituent (the oxygen atom) occupies the apical position.

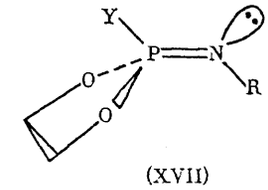
The analogous spiro-bi(triazaphospholes) (XIV) proved to be monomeric.[44] This can be explained both by the lower apicophilicity of nitrogen compared with oxygen and by the decrease of the electrophilicity of the phosphorus atom when oxygen is replaced by nitrogen:



(XVI)

## 2. Phosphazo-compounds with an Exocyclic P=N Bond

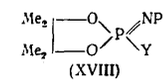
We shall now proceed to the consideration of 2-imino-1,3,2-dioxaphospholans and their derivatives—compounds with a five-membered phosphorus-containing heterocycle and an exocyclic P=N bond:



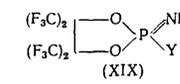
(XVII)

As in the acyclic PAC, the most stable conformation (XVII) is unsuitable for synchronous dimerisation. As a result of the decrease of the O—P—O angle and the increase of the P—O bond length on formation of the dioxaphospholan ring, the apicophilicity of the endocyclic oxygen atoms increases, while that of the exocyclic Y and N atoms correspondingly decreases. Thus, in contrast to azaphospholes, the presence of the ring induces a shortening and not a lengthening of the P=N bond. The stereoelectronic effect considered above obtains also in the dioxaphospholan ring. The hybridised LEP of one of the endocyclic oxygen atoms destabilises the antiperiplanar σ-bond of the other oxygen atom with phosphorus, which also contributes to the overall increase of the apicophilicity of these atoms. The phosphorus atom becomes more electrophilic overall and the basicity of the nitrogen atom falls somewhat. The relative probability of nucleophilic attack on the phosphorus atom from the side opposite to that of any one of the P—O bonds increases. Taking into account all these factors, one may conclude that, in terms of their tendency to dimerise, iminophospholans should occupy an intermediate position between azaphospholes and acyclic PAC with analogous substituents in the PA group. Experiments[45] agree satisfactorily with this conclusion.

The weak electron-donating effect of the alkyl substituents in the 4- and 5-positions in the heterocycle (XVIII) shifts the monomer–dimer equilibrium towards the monomer,[46] while the electron-accepting effect of the trifluoromethyl groups in the structure (XIX) causes a shift towards the dimer:[47,48]



(XVIII)

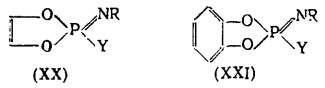


(XIX)

Compared with acyclic PAC, the influence of the steric factor of the substituent at the imino-nitrogen atom on the dimerisation is clearly reduced. Dimerisation is not interfered with even by the bulky groups at the nitrogen atom such as the trimethylsilyl or t-butyl groups. The role of the EO of the substituent Y is also weakened. X-Ray diffraction analysis of the dimer (XIX) with Y = F demonstrated the equatorial disposition of this substituent in the TBP of phosphorus,[47] which indicates a weaker apicophilicity of fluorine compared with the endocyclic oxygen atom—a result of which is improbable for acyclic phosphorane structures. On the other hand, the effect of the EO of the substituent at the nitrogen atom, which determines the nucleophilic properties of the latter, remains in force. The replacement of R = Ph by the $SO_2Ar$ group shifts the equilibrium towards the monomer.[46] An analogous situation obtains when R = Et is replaced by Ph even if Y = OMe is substituted simultaneously by the dimethylamino-group.

On passing from the dioxaphospholan ring (XVII) to the dioxaphospholen ring (XX), the shortening of the endocyclic C—C bond, caused by the increase of its multiplicity, is accompanied by a further decrease of the O—P—O angle and the increase of the P—O bond length. In addition, the LEP of the oxygen atoms are able to be conjugated with the

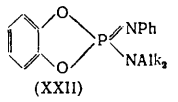
π-component of the C=C bond. Ultimately, the electron-accepting capacity of the ring and its tendency to dimerise increase.[49]



(XX) (XXI)

The replacement of the dioxaphospholan ring (XVII) by the benzodioxaphosphole ring (XXI) has an analogous effect. To demonstrate this, it is sufficient to compare data for the dimerisation of such compounds with R = Ph and Y = $NBu_2$, published by Gilyarov et al.[45] and Kukhar' et al.[50]

The influence of the electronic and steric factors on the dimerisation of *N*-arylimino-4,5-benzo-1,3,2-dioxaphospholes has been studied in detail.[51] The effect of the $NAlk_2$ group, which stabilises the monomeric form in iminodioxaphospholans,[45] is more than compensated in 2-dialkylamino-2-phenylimino-4,5-benzo-1,3,2-dioxaphospholes (XXII) by the increased apicophilicity of the endocyclic oxygen atoms:



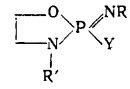
(XXII)

The compounds with Alk = Me or Bu exist only in the form of dimers. On the other hand, when Alk = Et, the monomer is detected in solution together with the dimer.[50] This difference can be accounted for by other, more refined effects of the stabilisation of the conformation of the PA group, which is unfavourable for dimerisation. For the analogous acyclic PAC, which exist only in the form of monomers, such effects can be neglected. The point is that, despite their low acidity, the hydrogen atoms in the C–H bonds are quite capable, under certain conditions, of interacting with the LEP of a powerful nucleophile such as the nitrogen atom of the PA group. Among compounds (XXII) with Alk = Me, Et, and Bu, the corresponding steric conditions for the formation of a weak intramolecular hydrogen bond can be realised only in the last two. The probability of a sufficiently close approach to the imino-nitrogen atom by one of the two β-methylene hydrogen atoms in the butyl group is smaller than for one of the three methyl groups when Alk = Et. Furthermore, the acidity of the methylene protons is smaller than that of the methyl protons.[52] As a result of all these factors, when Alk = Et, the stability of the hypothetical six-membered ring with the H...N hydrogen bond (and the "bonding" of the LEP of the imino-hydrogen in this bond) is a maximum and so is the probability of the existence of this compound in the monomeric form.

The replacement of the endocyclic oxygen atoms in the structure (XVII) by sulphur atoms, which are approximately equivalent as regards their apicophilic properties (although they are much less electronegative), should not be reflected in the monomer–dimer equilibrium. Indeed, like the analogous dioxaphospholans, 2-dimethylamino-2-phenylimino-1,3,2-dithiaphospholan is monomeric,[53] while 2-chloro-2-phenyl-imino-1,3,2-dithiaphospholan has a dimeric structure.[54] Hence it is clearly seen that the change in the electron-accepting properties of the ring does not by itself play a decisive role in the equilibrium considered and is reflected in the latter only in so far as the equilibrium is usually associated with the corresponding change in the apicophilicity of the endocyclic substituents at the phosphorus atom.

The effect of replacing one and even more so two endocyclic oxygen atoms by nitrogen atoms is interesting. Such compounds no longer exhibit a tendency to dimerise.[46,54–56]

It follows from the series based on the decreasing apicophilicity presented above that, for example, the apicophilicity of OR is greater than that of $NR_2$. For this reason, nucleophilic attack on phosphorus in the structure (XXIII) should proceed from the opposite side of the P–O bond.



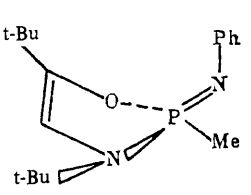
(XXIII)

However, it is noteworthy that the fixation of the O and N atoms in the almost planar oxazaphospholan ring entails some mutual approach of their apicophilicities. The stereoelectronic effect of the σ-LEP of the O atom weakens the endocyclic P–N bond, while the analogous effect for the P–O bond is absent owing to the orthogonality of the LEP of the N atom. The apicophilicity of the oxygen atom in the structure (XXIII) is therefore smaller than its apicophilicity in the dioxaphospholan ring, while the apicophilicity of the endocyclic nitrogen atom is greater than in the diazaphospholan ring, where the stereoelectronic effects are almost absent.

Furthermore, it has been shown[57,58] that the rupture of the endocyclic P–N bond in 1,3,2-oxazaphospholidines following nucleophilic attack on the phosphorus atom occurs with inversion of the configuration of the latter, which agrees with the hypothesis that the apical position in the TBP formed initially in the intermediate is occupied by nitrogen and not oxygen. The concept of the apicophilic capacity of the ligand, describing the probability of finding it on the same axis as the nucleophile during the attack of the latter on a tetracoordinate phosphorus atom, was therefore introduced. The apicophilic capacity of any ligand is assumed to depend on other substituents at the phosphorus atom, the nature of the nucleophile and the solvent, the presence of metal ions, and many other factors.[59]

Thus, although the endocyclic nitrogen atom is less apicophilic than the oxygen atom in the imino-derivatives of 1,3,2-oxazaphospholans (XXIII), it has a greater apicophilic capacity. This is caused by the presence of the bulky R′ substituent at this atom, located approximately in the O–P–N plane, as a result of which nucleophilic attack on the phosphorus atom along the P–O bond is hindered and the analogous attack from the opposite side of the P–N bond becomes more probable. A necessary condition for synchronous dimerisation is in this case the *cis*-disposition of the P–N and N–R bonds, which may be unattainable in the presence of bulky substituents at both nitrogen atoms. All these factors explain why PAC with oxaza- or diaza-phospholan rings lose their tendency to dimerise which is so characteristic of the dioxaphospholan ring.

3,5-Di(t-butyl)-2-methyl-2-phenylimino-1,3,2λ⁴-oxazaphospholine (XXIV) with the pseudoaxial disposition of the P=N bond is very characteristic in this sense:[56]

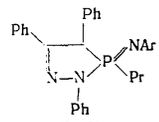


(XXIV)

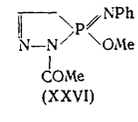
Even the presence of the endocyclic C=C double bond cannot ensure a stable dimeric structure of the above compound. The bulky t-butyl group in the 3- and 5-positions in the ring does not allow any of the endocyclic heteroatoms

to occupy the apical position in the phosphorus TBP of the hypothetical dimer. These causes, let alone the electron-donating properties of the exocyclic substituents at the phosphorus atom, are entirely sufficient to account for the exclusively monomeric structure of compound (XXIV).

In conformity with the principles described above, 1,2,3-diazaphospholine (XXV) [60] proved to be monomeric:



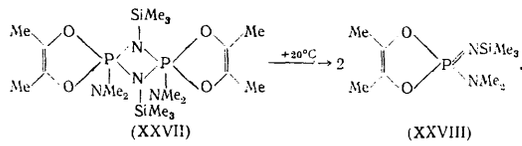
(XXV)



(XXVI)

This is caused by the low apicophilicity of the endocyclic nitrogen atom and the inadequate EO of the phenyl group at the phosphorus atom. On the other hand, compound (XXVI) with the analogous diazaphospholine ring is formed at the instant of synthesis together with its dimer, [61] which can be explained by the greater apicophilicity of the corresponding nitrogen atom as a consequence of the $\pi$-acceptor character of the exocyclic substituent at this atom, the greater apicophilic capacity of the latter, caused by the absence of the cumbersome phenyl group at the carbon atom in the 4-position in the ring, and also by the greater EO of the methoxy-group at the P atom compared with the phenyl group. Admittedly, the location of the most apicophilic substituent (OMe) in the apical position of the phosphorus TBP requires the energetically unfavourable diequatorial disposition of the diazaphospholine ring. For this reason, only the monomeric form remains after five days storage in the form of a solution in bromoform.

An analogous situation has been described by Zeiss. [62] The crystalline diazadiphosphetidine (XXVII) isolated at a low temperature (−78 °C) is fully converted into the monomeric form (XXVIII) after dissolution in acetonitrile and storage for 24 h at room temperature:



(XXVII) (XXVIII)

At +20 °C the dioxaphospholen (XXVIII) is a colourless liquid, which crystallises at −27 °C, but cannot be reconverted into the dimeric form (XXVII). The thermodynamic stability of the dimer (XXVII) in relation to the monomer (XXVIII) can be explained both by the bulky nature of the trimethylsilyl group at the imino-nitrogen atom and by the electron-donating capacity of the exocyclic dimethylamino- and methyl groups in the five-membered ring. [62]

---o0o---

Summarising, one should note that all the main factors determining the dimerisation of PAC and influencing the position of the monomer–dimer equilibrium are now well known. The so-called phospholan effect, which until recently had an aura of being "unexplained", can be accounted for on the basis of general ideas about the reactivity of the tetracoordinate phosphorus atom and about the electronic nature of the PA group.

All this makes it possible not only to explain but also to shift in the required direction the monomer–dimer equilibrium involving the PAC synthesised by altering appropriately the electronic and (or) steric properties of the substituents at the P and N atoms in the PA group. [26]

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# Applied Aspects of the Chemistry of the Porphyrins

O.A.Golubchikov and B.D.Berezin

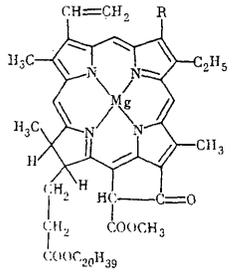
The review deals with the prospects for the practical application of porphyrins as catalysts and reactants in various chemical, electrochemical, and photochemical processes.
The bibliography includes 347 references.

CONTENTS

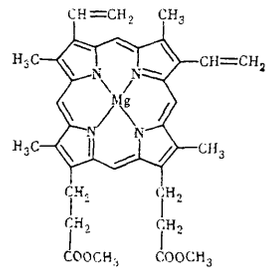

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## I. INTRODUCTION

Porphyrin complexes play an important role in nature. It is sufficient to quote the example of chlorophyll [MgChl (I)], which, forming part of the composition of chloroplasts, effects photosynthesis, and haem [FePP (II)], which, as a component of haemoglobin, transports oxygen to animal tissues, as a component of myoglobin, it ensures its storage, and, as a component of cytochromes, it catalyses biochemical oxidation–reduction reactions. There is no doubt that the primary stimulus which led to the investigation of porphyrins and their metal complexes was provided precisely by the biocatalytic properties of metalloporphyrins. This stimulus still remains important.



chlorophyll *a*, with R = $CH_3$;
chlorophyll *b*, with R = CHO
(I)

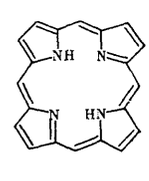


protohaem (II)

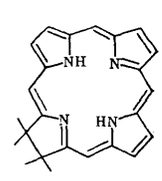
During the last 20–25 years, there has been a sharp growth of interest in porphyrins. Together with fundamental theoretical investigations, numerous applied studies have been made. Porphyrins proved to be universal catalysts of many chemical, electrochemical, and photochemical reactions.

The high catalytic activity of porphyrins is due to the aromatic character of the conjugated π-system of the macroring, the conjugation of the coordinated metal atom to the π-system of the ligand, and the ease with which the oxidation state of the central metal atoms, for example, those of Co, Fe, Mn, and others, changes. It is also important that the extensive π-electron systems of porphyrins have a distinct electron-buffer character. Depending on the other reactant, porphyrins can exhibit both electron-donating and electron-accepting properties. It is significant that porphyrins are chemically stable in the ground and photoexcited states and also in the form of radical-cations and radical-anions. The unique properties of the porphyrins can serve as a basis for the solution of many problems of practical importance.

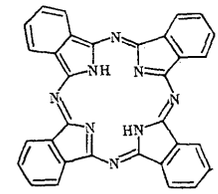
In this review the term porphyrin is used in a wide sense. Porphyrins ($H_2P$) are assumed to include porphin ($H_2Po$) (III), chlorin ($H_2Ch$) (IV), phthalocyanine ($H_2Phc$) (V), and their derivatives and metal complexes (MP). Tetraphenylporphins ($H_2TPhPo$) ($X_4$) (VI) and tetrabenzoporphins $H_2TBPo$ ($X_4$) (VII) are important among the $H_2Po$ derivatives.



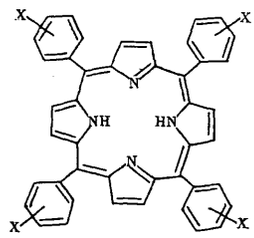
porphin (III)



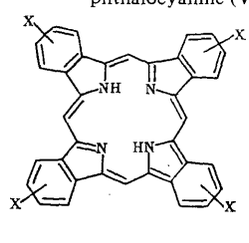
chlorin (IV)



phthalocyanine (V)



tetraphenylporphin (VI, X = H)
and its derivatives



tetrabenzoporphin (VII, X = H)
and its derivatives

The principle applications of the porphyrin are listed in Table 1.

## II. CATALYSIS OF ELECTROCHEMICAL PROCESSES

Metalloporphyrins are widely investigated and used as catalysts of electrochemical oxidation-reduction reactions. Most studies in this field concern the catalysis of the reduction of molecular oxygen in low-temperature fuel cells. The catalytic activity of metal complexes of porphyrins in the cathodic reduction of oxygen was first observed by Jasinski:[1-3]

$$O_2+4H^++4e^-\rightarrow 2H_2O\ . \qquad (1)$$

A large number of publications on this topic soon appeared.[4-59] There are two reviews on the cathodic reduction of oxygen.[10,11]

Table 1. Practical applications of porphyrins

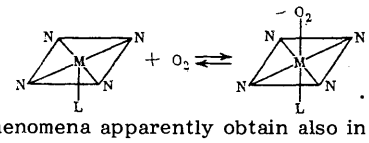
| Application | References |
|---|---|
| Catalysis of cathodic reduction of oxygen | [1-59] |
| Catalysis of anodic oxidation of sulphur dioxide | [60-65] |
| Catalysis of cathodic reduction of hydrogen peroxide | [11, 66] |
| Catalysis of cathodic reduction of carbon dioxide | [67, 68] |
| Catalysis of cathodic reduction of nitrous oxide | [69] |
| Catalysis of electrochemical synthesis of organic compounds | [70, 71] |
| Catalysis of oxidation of hydrogen sulphide, mercaptans, and other sulphur derivatives | [72-90] |
| Catalysis of decomposition of hydrogen peroxide | [42, 91-105] |
| Catalysis of decomposition of organic peroxides | [106-113] |
| Catalysis of oxidation of hydrocarbons | [114-138] |
| Catalysis of oxidation of alcohols and phenols | [98, 99, 135, 137, 139-151] |
| Catalysis of oxidation of aledhydes and carboxylic acids | [99, 129, 137, 148, 149, 152-157] |
| Catalysis of oxidation of carbon monoxide | [158, 159] |
| Catalysis of reduction of organic compounds | [160-163] |
| Catalysis of oxidation and reduction reactions of nitrogen-containing compounds | [142, 160, 164-169] |
| Catalysis of polymerisation and regulation of degree of polymerisation | [170-180] |
| Catalysis of isomerisation of unsaturated compounds | [181-188] |
| Three-dimensional phase holography | [189-190] |
| Catalysis of photochemical decomposition of water | [191-215] |
| Catalysis of photoelectrochemical reactions | [216-239] |
| Semiconductors and photosemiconductors | [222-224, 236, 240-293] |
| Electrochromic materials | [294-299] |
| Pigments, dyes, and food dyes | [300, 301] |
| Enrichment of radioisotopes | [99, 302-315] |
| Analytical chemistry | [316-347] |
| Other applications | |

Oxygen is usually reduced in fuel cells in a highly acidic or highly alkaline medium under the conditions of an appreciable polarisation of the cathode. For this reason, one of the central problems in the development of catalysts for the electrochemical reduction of oxygen is the problem of corrosion resistance.

The investigations have shown[1-59] that, apart from noble metals, whose applicability is limited, metalloporphyrins can serve as active and stable catalysts of reaction (1). The catalytic activity of MP depends on a number of factors, among which the nature of the coordinated metal atom proved to be the most important. Among tens of MP investigated, iron,[10,11,30,35,37] cobalt,[11,25,55] and ruthenium and iridium[45] complexes exhibit the greatest activity. The nature of the porphyrin ligand has a smaller effect on the catalytic activity. However, the increase of the activity of the catalyst with increase of the size of the conjugated $\pi$-bond system of the porphyrin has been demonstrated. Polymeric phthalocyanines $(MPhc)_i$ are less active than the monomeric compounds.[11,15-17,25,33,35,36,43] There exist contradictory views about the electronic effect of the substituents in porphyrins. It was concluded[10,11,25,59] that electron-donating substituents activate the catalyst, while Been et al.[45] claimed that they deactivate it.

In the practical application of reaction (1) in fuel cells, the MP, whose electrical conductivity is low, are deposited on various conducting carriers. Metals and carbonaceous materials (graphite, carbon black, activated charcoal) have been investigated as carriers. Metalloporphyrins deposited on carbonaceous materials show the highest activity.

The catalytic activity of MP in reaction (1) is closely related to their ability to bind oxygen reversibly. The extracoordination of $O_2$ to MP entails partial transfer of electron density from the central metal atom to the antibonding $\pi$ orbital of oxygen. Thus the extracoordination constitutes the initial stage in the reduction of $O_2$. The stability of oxygen extracomplexes of MP is determined by the nature of the second, *trans*-extraligand L:



(2)

Analogous phenomena apparently obtain also in the electrochemical reduction of $O_2$. The functional groups on the surface of the carrier fulfill the role of the extraligand. Chemical modification of the surfaces of carbonaceous carriers therefore constitutes one of the most promising ways of increasing the activity of porphyrin catalysts of the cathodic reduction of molecular oxygen.

One of the most important applications of porphyrins is catalysis of the anodic oxidation of sulphur dioxide. Studies in this field have begun to develop during the last 5–7 years in connection with the research into the problems of atomic-hydrogen power engineering.[60-65]

There exist various projects for the manufacture of hydrogen from water. The thermoelectrochemical sulphuric acid method, in which hydrogen is obtained in two stages, is closest to practical realisation. In the first stage, sulphuric acid is subjected to catalytic thermal dissociation by the heat of a nuclear reactor:

$$2H_2SO_4\rightarrow O_2+2H_2O+2SO_2\ . \qquad (3)$$

In the second stage sulphur dioxide is electrochemically oxidised after its separation from oxygen and water. Hydrogen is evolved at the cathode and is used as the fuel:

$$SO_2+2H_2O-2e^-\rightarrow H_2SO_4+2H^+\ ; \qquad (4)$$

$$2H^++2e^-\rightarrow H_2\ . \qquad (5)$$

The normal electrode potential of reaction (4) is 0.17 V, which makes it possible, in principle, to obtain fairly cheap hydrogen. However, under real conditions, the sulphur dioxide oxidation reaction is accompanied by intense anodic polarisation. For example, the oxidation of $SO_2$ on carbonaceous materials proceeds at an appreciable rate only at potentials in excess of 0.8 V.[64] Reaction (4) takes place under very severe conditions: in concentrated sulphuric acid at an elevated temperature and under the conditions of appreciable anodic polarisation. Thus fuel hydrogen can be obtained in the thermoelectrochemical sulphuric acid cycle subject to the condition that highly active catalysts of the anodic oxidation of sulphur dioxide, which at the same time possess a high chemical stability, are found. Until recently, only one catalyst meeting the above requirements was known: metallic platinum in a pure state or deposited on carbonaceous carriers.[60] Investigations[61-65] have shown that metalloporphyrins deposited on carbonaceous carriers are effective catalysts of the anodic oxidation of $SO_2$. Fig. 1 presents the polarisation curves for the oxidation of sulphur

dioxide. Evidently, the activity of CoTPhPo(p-$OCH_3$)$_4$ is comparable to that of the platinum catalyst. It is significant that the activity and stability of MP-based catalysts increase sharply as a result of heat treatment at 900–1000 K.

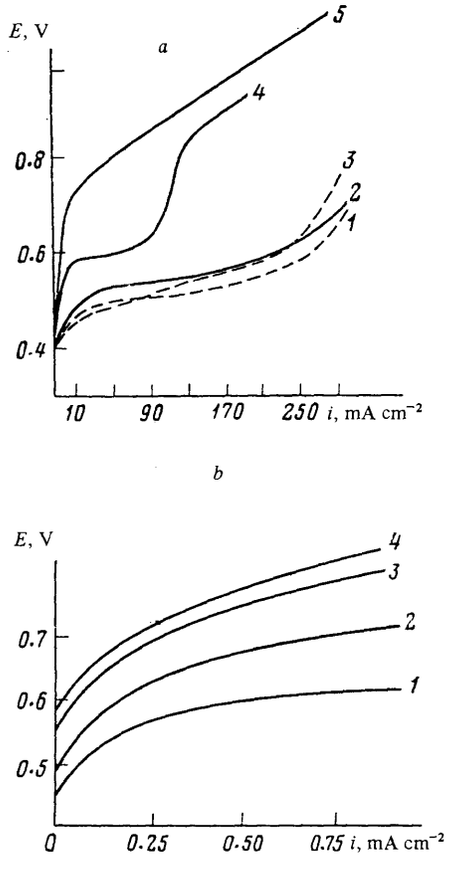



**Figure 1.** Polarisation curves for the oxidation of $SO_2$ in sulphuric acid electrolytes: *a*) on porous PG-50 graphite anodes heat-treated at 1020 K and activated by different substances [*1*) CoTPhPo(*p*-$OCH_3$)$_4$; *2*) Pt; *3*) NiTPhPo.(*p*-$OCH_3$); *4*) FeTPhPo(*p*-$OCH_3$); *5*) without catalyst[64]]; *b*) pyrographite anodes activated by different substances [*1*) CoTPhPo; *2*) CoTPhPo(*p*-$OCH_3$)$_4$; *3*) CoPhc; *4*) without catalyst[65]].

The catalytic activity of MP in the anodic oxidation of sulphur dioxide is determined by the nature of the porphyrin ligand and the metal atom. Metal-free porphyrins are inactive in the oxidation of $SO_2$. The copper complexes and other metalloporphyrins are almost inactive. The catalytic activity of the heat-treated CoTPhPo(*p*-$OCH_3$)$_4$ is higher than that of CoTPhPo.

It is noteworthy that the catalysis of the electrochemical oxidation of $SO_2$ has been investigated for heat-treated specimens. The nature of the chemical transformations of $H_2P$ and MP in the high-temperature treatment is insufficiently clear. It is therefore impossible to formulate at present unambiguous conclusions about the effect of the structure of the porphyrin ligands on the catalytic activity of the MP in the anodic oxidation of sulphur dioxide.

Among other electrocatalytic processes occurring with participation of MP, mention may be made of the cathodic reduction of hydrogen peroxide,[11,66] carbon dioxide,[67,68] nitrous oxide,[69] and organohalogen derivatives.[70,71] The study of the cathodic reduction of hydrogen peroxide is important in connection with the development of oxygen and air electrodes, since hydrogen peroxide is an intermediate in the reduction of oxygen. It has been established that in alkaline electrolytes iron- and cobalt-phthalocyanines exhibits a high activity, which increase in the sequence CoPhc < FePhc < $(CoPhc)_i$.[11] Protohaem is an effective catalyst of the cathodic reduction of $H_2O_2$.[66]

Metalloporphyrins catalyse the electrochemical reduction of carbon dioxide.[67,68] Methanol, formic and oxalic acids, and other valuable compounds have been found among the reduction products. The practical application of this reaction is a matter for the remote future, since the reduction process requires a large energy expenditure.

The catalytic activities of several cyclophan dimers of cobalt-porphyrins in the cathodic reduction of nitrous oxide have been investigated.[69] The reduction proceeds with formation of molecular nitrogen. The dimers investigated are much more active than the monomeric complexes. The authors[69] suggest that the reduction proceeds via a two-electron concerted mechanism.

The catalysis of the electrochemical synthesis of organic compounds may be a promising application of MP.

Methods have been developed[70,71] for the chemical modification of the surfaces of electrodes made of carbonaceous materials by the covalent binding of MP based on $H_2$TPhPo.(*p*-$NH_2$)$_4$. It has been shown that the cathodic reduction potentials of a series of halogeno-derivatives of organic compounds on the modified electrodes are lower by approximately 1 V than on the unmodified electrodes.

## III. CATALYSIS OF OXIDATION-REDUCTION REACTIONS

A very important practical application of porphyrins is the catalysis of the oxidation of hydrogen sulphide and mercaptans (RSH) by atmospheric oxygen. This process is used to purify the waste water from petroleum distilleries and non-ferrous metallurgical undertakings and for the removal of sulphur from petroleum products and natural gas. Mercaptans and similar compounds are oxidised to dialkyl disulphides:

$$4RSH+O_2 \rightarrow 2RSSR+2H_2O \quad . \qquad (6)$$

At the end of the 1950s and the beginning of the 1960s it was observed[72] that the porphyrin complexes of cobalt and vanadium as well as their sulphonate and carboxylate derivatives catalyse the oxidation of mercaptan sulphur by atmospheric oxygen in aqueous alkaline solutions. This process has been used to purify petroleum distillates. Mercaptans are oxidised under the conditions of homogeneous catalysis. In the homogeneous-catalytic oxidation, the hydrocarbon distillate is treated with an aqueous solution of alkali (2–50% NaOH) containing ~0.5% of the catalyst, usually the CoPhc sulphonate. After the extraction of the mercaptans and separation of the aqueous and organic phases, the mercaptides are oxidised by blowing atmospheric oxygen into the aqueous solution. The dialkyl disulphides rising to the surface are separated and the regenerated solution of the alkali and the catalyst is again directed to the extraction of mercaptans. The heterogeneous version of the purification

process differs from that described above by the use of a catalyst adsorbed on an appropriate carrier, usually on activated charcoal.

The catalysis of the oxidation of hydrogen sulphide, mercaptans, and similar compounds has been investigated mainly on metallophthalocyanines. Metalloporphyrins have been investigated in this reaction to a lesser extent, although it is known[72,76] that derivatives of CoTPhPo are catalytically active. The catalytic activity of MPhc depends in many respects on the nature of the central atom. For example, the effectiveness of the catalysis in the oxidation of hydrogen sulphide by atmospheric oxygen increases in the following sequence:[73]

$$\underset{0.30}{\text{ZnPhcTS}} < \underset{0.46}{\text{CuPhcTS}} < \underset{2.9}{\text{V(O)PhcTS}} < \underset{17.3}{\text{NiPhcTs}} < \underset{140}{\text{FePhcTS}} < \underset{5600}{\text{CoPhcTS}}.$$

Here MPhcTS is the tetrasulphonic acid of the metallophthalocyanine. The catalytic activities, measured in moles of absorbed $O_2$ per mole of the catalyst per minute, are indicated under the formulae. A series close to that quoted above has been obtained[77] in the homogeneous oxidation of propanethiol:

$$\text{Cr(Cl)PhcDS} < \text{ZnPhcDS} < \text{Al(Cl)PhcDS} < \text{Sb(Cl)PhcDS} < \text{NiPhcDS} < \\ < \text{FePhcDS} < \text{CuPhcDS} < \text{CoPhcDS}.$$

Here MPhcDS is the disulphonic acid of the metallophthalocyanine. The cobalt complexes show the highest activity in aqueous solutions of alkalis.

The structure of the ligand also has a significant effect on the rate of oxidation of mercaptans and hydrogen sulphide. The following catalytic activity series has been obtained for CoPhc derivatives:[74]

$$\underset{1.67\ (2.74)}{\text{CoPhc}(SO_3Na)_4Cl_4} > \underset{1\ (1)}{\text{CoPhc}(SO_3Na)_4} > \underset{0.2\ (0.5)}{\text{CoPhc}(SO_3Na)} > \underset{0.07\ (0.23)}{\text{CoPhc}(SO_3Na)_8} > \\ > \underset{0.02\ (0.062)}{\text{CoPhc}(SO_3Na)_4(COOH)_4}.$$

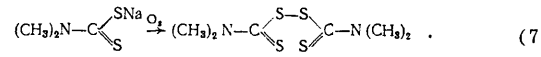
The relative rate constants for the oxidation of cysteine and hydrogen sulphide are indicated under the formulae, the values in brackets referring to the latter; the rate constants for the reactions on $CoPhc(SO_3Na)_4$ were assumed to be unity. It has been established in recent years[77-80] that the catalytic activity of the cobalt-phthalocyanine-sulphonic acids increases greatly when strongly electron-donating (OH, $NH_2$) and electron-accepting ($NO_2$) substituents are introduced into the catalyst molecule. For example, the following series has been quoted.[77]

$$\text{CoPhc}(SO_3Na)_2 < \text{CoPhc}(SO_3Na)_2(NO_2)_4 < (\text{CoPhc})_i < [\text{CoPhc}(SO_3Na)_2]_i < \\ < \text{CoPhc}(SO_3Na)_2(OH)_4 < \text{CoPhc}(SO_3Na)_2(NH_2)_4.$$

Further progress in this field is expected in three directions. Firstly, studies on the structural modification of porphyrin ligands in order to increase the catalytic activity of their metal complexes are promising. Secondly, the development of methods for the activation of heterogeneous catalysts for the oxidation of mercaptans constitutes an urgent problem. In this connection interesting patents have been taken out.[81-85] These describe procedures in which the activation of the MPhc adsorbed on activated charcoal is attained by modifying the carrier with the aid of tetraalkylammonium salts $(R_4N)^+X^-$ containing bulky organic groups R. Methods have also been developed for the immobilisation of complexes of $H_2$TPhPo and its derivatives[76] and MPhc[90] on the surfaces of polymeric carriers. The catalytic activity of the modified polymers[76,90] in the oxidation of alkanethiols has been demonstrated. Thirdly, the replacement of aqueous solutions by non-aqueous solutions may prove to be promising in the field of the elimination of sulphur. Thus, when dimethylformamide (DMF) was used as the solvent, it was possible to achieve the selective oxidation of hydrogen sulphide to elemental sulphur.[88] In aqueous solutions the most active catalysts of the oxidation of mercaptans and hydrogen sulphide are the cobalt complexes, whereas in organic solvents the porphyrin complexes of iron are more effective. The following catalytic activity series has been established for phthalocyaninetetrasulphonic acid derivatives:[88] Fe > Co > Zn > Cu > Al > Cr.

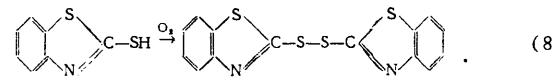
In toluene solution Fe(Cl)TPhPo catalyses the oxidation of alkanethiols by atmospheric oxygen, the addition of pyridine having an appreciable activating effect on the catalyst.[89]

The sulphonic acids of CoPhc and their derivatives with substituents in the benzene ring can be used in the synthesis of certain sulphur-containing accelerators of the vulcanisation of raw rubber. The catalytic activity of CoPhc derivatives in the oxidation of *NN*-dimethyldithiocarbamate has been demonstrated:[78,80]



(7)

The catalytic oxidation of 2-mercaptobenzothiazole has been investigated:[79]



(8)

It has been shown[78,79] that the tetrahydroxy-, tetra-amino-, and tetranitro-derivatives exhibit a high catalytic activity among phthalocyaninedisulphonic acids.

In conclusion one should note that the oxidation of hydrogen sulphide and mercaptans by atmospheric oxygen can take place in the gas phase at temperatures in the range 470–620 K.[86,87] The metal complexes of phthalocyanine catalyse this process. In the oxidation of hydrogen sulphide the catalytic activity of polymeric phthalocyanines varies in the following sequence as a function of the nature of the metal: Fe > Co > Cu > Mn.[86] The activity series of the monomeric complexes has been obtained in the oxidation reaction of isopropanethiol: Fe > Cu > Mn > Co > Zn > Ni.[87]

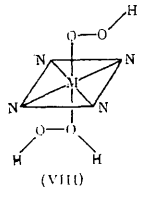
Numerous studies[91-103] have been devoted to the catalytic activity of MP in the disproportionation of hydrogen peroxide:

$$2H_2O_2 \rightarrow 2H_2O + O_2 . \qquad (9)$$

These investigations are important for the protection of plants and animals against the $H_2O_2$ formed as a result of their vital activity. In living organisms hydrogen peroxide is decomposed with the aid of haem-containing enzymes—catalases. The structure, properties, and the mechanism of the activity of catalases have been discussed in detail in a monograph.[104] The catalase activity of MP has also been investigated in connection with the development of oxygen cells in which $H_2O_2$ is formed as an intermediate in the cathodic reduction of molecular oxygen.[11]

MP exhibits a catalase activity under both homogeneous and heterogeneous conditions. The catalytic activity is determined mainly by the nature of the metal atom. It has been established[92] that, under the conditions of heterogeneous catalysis, the highest activity is shown by the osmium, ruthenium, and iron complexes of $H_2$Phc. The catalytic activity of MPhc with other metals is lower by at least two orders of magnitude. The catalysis of reaction (9) by metal complexes of phthalocyanine deposited on carbonaceous carriers has been investigated[100] and it has been shown that the catalytic activity depends significantly on

the nature of the carbonaceous carrier. Depending on the nature of the central metal atom in the monomeric phthalocyanines adsorbed on the carbonaceous carriers, the activity falls in the sequence: Os ≫ Fe > Ru > Pt > Rh > Pd, Ir whereas for polymeric phthalocyanines under the same conditions we have: Fe > Os > Pt, Ru > Ir, Rh, Pd; Fe > Co ≫ Ni > Cu.[100] It is important to note that, when individual heterogeneous phthalocyanine catalysts are used, the polymeric complexes have no advantages over the monomeric complexes.[94,105] On the other hand, the metallophthalocyanine polymers adsorbed on carriers are significantly more active than the monomers.[100] The fact that the activities of both homogeneous and heterogeneous catalysts change on formation of extracomplexes of metallophthalocyanines is important for the development of ideas about the mechanism of the catalytic decomposition of hydrogen peroxide. Small amounts of added extraligands such as pyridine, imidazole, and triphenylphosphine activate the catalyst[11] evidently as a result of the formation of pentacoordinated complexes. An appreciable excess of the extraligand suppresses the catalytic activity,[92] apparently as a consequence of the formation of hexacoordinated extracomplexes. The facts listed above are inconsistent with the mechanism of the catalytic decomposition of hydrogen peroxide based on the hypothesis that hexacoordinated extracomplexes of metalloporphyrin (VIII) with two hydrogen peroxide molecules are formed.[101,103]



(VIII)

Metalloporphyrins catalyse the decomposition of organic hydroperoxides ROOH.[106–113] This reaction constitutes an important link in the catalytic oxidation of hydrocarbons on MP and is therefore considered to some extent in all studies devoted to this question. In contrast to the hydrogen peroxide disproportionation reaction, which apparently takes place without the formation of free radicals, organic hydroperoxides are decomposed via a radical mechanism. The porphyrin and phthalocyanine complexes of metals such as cobalt, iron, nickel, and manganese are effective catalysts of the decomposition of the peroxides. In discussing the reaction mechanism, the authors[108–111] assume that the central metal atom is the active centre of the catalyst. On the other hand, in other studies[106,112] it has been suggested that the hydroperoxide decomposition reaction can take place on the periphery of the MPhc molecule, for example, via the formation of a hydrogen bond between the molecule and one of the peripheral nitrogen atoms. The second reaction pathway appears less likely, since it is known that the complexes of porphyrins themselves, which have no peripheral nitrogen atoms, exhibit a high catalytic activity in the reaction considered. It has been established[113] that organic peroxides form fairly stable extracomplexes with CoTPhPo. The authors[113] noted a significant role of the extracoordination in the decomposition of ROOH.

Extensive studies have been made on the utilisation of MP as the catalysts of the oxidation of hydrocarbons by atmospheric oxygen. The catalytic activities of MP and MPhc in the oxidation reactions of cumene, ethylbenzene, propene, cyclohexane, tetralin, indoles, and other compounds have been studied. A review has been published on this subject.[114] Hydrocarbons are oxidised via a radical chain mechanism and the reaction involves the intermediate formation of hydroperoxides which serve as autocatalysts of the oxidation process. Systematic investigations of the autocatalytic oxidation of cumene and certain other hydrocarbons have been described.[115–120] It has been established that below 370 K the main cumene oxidation product on the phthalocyanine complexes of copper, nickel, magnesium, and tin is the hydroperoxide, whose yield exceeds 90% under these conditions. Hydrocarbon hydroperoxides decompose catalytically on iron and cobalt complexes at the usual temperatures and on virtually all the MPhc investigated at high temperatures (420 K and above) with formation of the final oxidation products.

The catalytic activity of MPhc has been explained[115–120] by the activation of molecular oxygen as a result of extracoordination. The extracoordination of oxygen is accompanied by the transfer of electron and spin density from the central metal atom of the catalyst to oxygen:

$$\mathrm{MPhc} + \mathrm{O_2} \rightarrow \mathrm{MPhc}^{\delta+} \ldots \mathrm{O}^{\delta-} \quad . \tag{10}$$

The coordinated oxygen has radical properties and is therefore capable of abstracting a hydrogen atom from the hydrocarbon molecule:

$$\mathrm{RH} + \mathrm{MPhc}^{\delta+} \ldots \mathrm{O_2^{\delta-}} \rightarrow \mathrm{R^{\cdot}} + \mathrm{HO_2^{\cdot}} + \mathrm{MPhc}; \tag{11}$$

$$\mathrm{R^{\cdot}} + \mathrm{O_2} \rightarrow \mathrm{ROO^{\cdot}} \quad ; \tag{12}$$

$$\mathrm{ROO^{\cdot}} + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R^{\cdot}} \; ; \tag{13}$$

$$\mathrm{ROO^{\cdot}} \rightarrow \text{other oxidation products.} \tag{14}$$

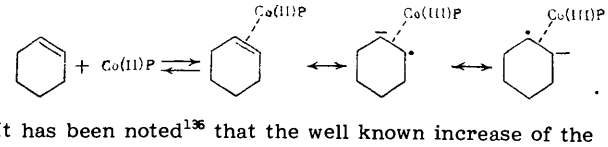
At high temperatures the oxidation of hydrocarbons proceeds autocatalytically. The catalytic decomposition products of the hydroperoxides serve as the source of free radicals:

$$\mathrm{MPhc} + \mathrm{ROOH} \rightarrow \mathrm{MPhc^{+}} + \mathrm{RO^{\cdot}} + \mathrm{OH^{-}}; \tag{15}$$

$$\mathrm{MPhc^{+}} + \mathrm{ROOH} \rightarrow \mathrm{MPhc} + \mathrm{ROO^{\cdot}} + \mathrm{H^{+}}; \tag{16}$$

$$\mathrm{RO^{\cdot}} + \mathrm{RH} \rightarrow \mathrm{ROH} + \mathrm{R^{\cdot}} \; . \tag{17}$$

Next the oxidation reaction proceeds in accordance with Eqns.(12)–(14). It is noteworthy that a careful study of the kinetics of the oxidation of cumene containing minimal amounts of hydroperoxides has led to the conclusion[134] that the Cu, Zn, Ni, V, and Mg complexes of tetra-t-butylphthalocyanine at 330–350 K catalyse the oxidation of cumene via the decomposition of cumenyl hydroperoxide and not via the activation of oxygen. The activation of oxygen has also been ruled out in studies[122,124,125] of the catalytic oxidation of cyclohexene and squalene on iron(II), cobalt(II), and cobalt(III) complexes of protoporphyrin and octaethylporphin. It has been suggested[122,123,125] that the catalytic activity of the MP is due to the activation of the double bond via the transfer of spin density from the central metal atom to the double bond of the extracoordinated alkene, for example:

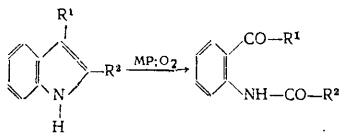



(18)

It has been noted[136] that the well known increase of the selectivity of the oxidation of alkenes in the presence of MPhc with a simultaneous increase of the induction period

of the reaction indicates unambiguously that the mechanism of the catalytic activity consists in the catalysis of the interaction of hydroperoxides or hydroperoxy-radicals with the olefin.

As a consequence of the radical mechanism, the autoxidation reactions of hydrocarbons have a low selectivity. For example, the liquid-phase oxidation of propene on the phthalocyanine complexes of Mo, V, Sn, and Ru (individual and adsorbed on various carriers) involves the formation, together with the target product (epoxypropane), also of acetaldehyde, isopropyl alcohol, acetone, methyl formate, and other products.[136] The yield of epoxypropane does not exceed 45%. In the oxidation of cyclohexene, the main products are the corresponding epoxy-derivative, cyclohexenol, and cyclohexenone. In some cases the oxidation proceeds with a fairly high selectivity. Thus the oxidation of substituted indoles on the cobalt(II), cobalt(III), and manganese(III) complexes of $H_2TPhPo$ and deuterioporphyrin ($H_2DPo$) affords a satisfactory yield of the corresponding ketoamides:[126,127]

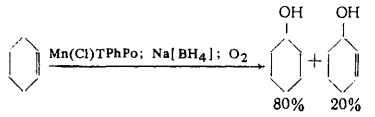


(19)

The catalytic activity series has been established in the oxidation reaction of skatole: CoDPo > CoTPhPo ≫ CuTPhPo ≫ NiTPhPo ≅ 0.[126]

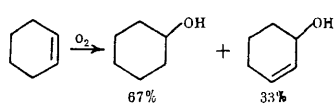
The practical employment of MP for the oxidation of hydrocarbons is complicated by the rapid poisoning of the catalyst as a result of the irreversible oxidation of the MP by alkylperoxy-radicals. Studies where a significant stabilisation of porphyrin catalysts after approximately equimolar amounts (relative to the MP) of copper acetylacetonate had been added are of interest in this respect.[122,124]

An interesting reaction involving the selective oxidation of alkenes to alcohols on treatment with molecular oxygen, tetrahydroborate, and the Mn(Cl)TPhPo catalyst has been discovered recently.[128,130,131,133] The oxidation of cyclohexene has been studied:[133]

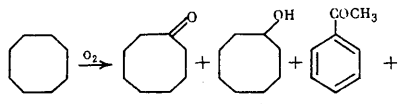


(20)

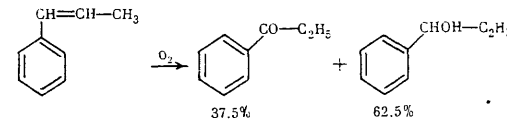
The mechanism of this reaction differs from the usual radical autoxidation, since the reaction has no induction period and is not inhibited by 2,6-di-t-butylphenol. It is noteworthy that the oxidation process proceeds under very mild conditions: at room temperature and normal pressure, and is much faster than radical autoxidation. It has been concluded[133] that the main reaction pathway involves the formation of epoxycyclohexane, which is then reduced by the excess tetrahydroborate to cyclohexanol. The study of the oxidation of alkenes in the Mn(Cl)TPhPo–$[Bu_4N]^+[BH_4]^-$–$O_2$ ternary system[130] yielded the following results:



(21)



(22)



(23)

It was concluded that under these conditions the alkenes are oxidised selectively with formation of ketones and the latter are reduced by the excess tetrahydroborate to alcohols. In their study of the oxidation of alkenes of different structure by atmospheric oxygen in the presence of Mn(Cl)TPhPo and $NaBH_4$, Enikolopov and co-workers[128,131] established that the rate of reaction increases as the alkyl substituents at the double bond accumulate. The oxidation proceeds selectively with respect to the most substituted hydrogen atom. The data obtained for the oxidation of steroids demonstrate unambiguously that neither ketones nor epoxides can be intermediates in the oxidation reaction. The authors[128,131] suggest that the oxidation intermediate is a complex of the olefin, the activated oxygen, and Mn(II).TPhPo. Depending on the nature of the olefin, the complex can disproportionate to a ketone or can be reduced by the tetrahydroborate to the alcohol.

The metal complexes catalyse the autoxidation of alcohols with phenols,[98,99,135,139–151] aldehydes, and carboxylic acids.[99,129,137,148,149,153–157] The reaction has a radical chain mechanism. The aldehyde oxidation products are peracids or carboxylic acids. Phenols are oxidised to the corresponding quinones and other products. Carboxylic acids undergo oxidative decarboxylation. Studies in this field have been surveyed in monographs.[11,112]

The method of synthesis of aromatic aldehydes RCHO from a wide variety of compounds of the type $RCH_2X$ (X = OH, OR, $NH_2$, etc.), described by Tabushi and Koga,[145] is of great interest to organic chemists concerned with synthesis. Manganese(IV) complexes of haematoporphyrin ($H_2HaePo$) or $H_2TPhPo$, obtained directly in the reaction system by the oxidation of manganese(III) complexes with sodium hypochlorite, are used as the oxidants. The reaction can be carried out also in a catalytic version. With the aid of Mn(IV)P, the oxidative cleavage of the ether linkage, for example in benzyl methyl ether, goes to completion at room temperature in 1 min, after which the oxidation proceeds selectively to give benzaldehyde.

A method of synthesis of MPhc, dispersed unimolecularly in zeolite matrices, has been developed.[151] With the aid of catalysts of this type based on CuPhc, CoPhc, and NiPhc, it is possible to carry out a very interesting reaction involving the oxidation of carbon monoxide by atmospheric oxygen. It is significant that the oxidation proceeds very rapidly even at 195 K.[158] The importance of this process for the protection of the environment is evident. However, the proposed catalysts[158] are very rapidly poisoned, apparently by carbon dioxide or carbonate ions.

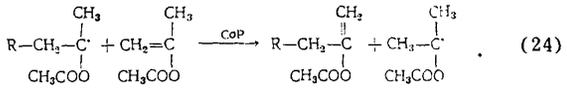
The catalysis of the electrochemical oxidation of carbon monoxide on metal complexes of octaethylporphin ($H_2OEPo$), $H_2TPhPo$, $H_2TBPo$, and $H_2Phc$ has been studied[159] and it has been established that IrTPhPo and RhTPhPo are active in acid and alkaline media. The iron and cobalt complexes exhibit an appreciable activity in alkaline solutions. It has been noted[159] that the catalytic activities of the iron complexes increase in the sequence FeTBPo < FeOEPo < FeTPhPo.

MP exhibit a catalytic activity not only in oxidation reactions but also in the reduction and photochemical reduction of organic compounds. The catalytic activity of CoTPhPo.$(p\text{-}SO_3H)_4$ in the hydrogenation of acetylene[160] and of the MPhc radical anions in the hydrogenation of alkenes[161–163] has been demonstrated. The high-temperature (373–573 K) hydrogenation–dehydrogenation reactions of alcohols and aldehydes in the presence of MPhc have been investigated.[141]

A number of studies of the catalytic oxidation–reduction reactions of nitrogen-containing compounds have been described in the literature. The report[160] of the catalytic activity of $CoTPhPo(SO_3H)_4$ in the reduction of molecular nitrogen by sodium tetrahydroborate is the most interesting in this field. The catalytic activity of MP in the oxidation of hydrazine and hydroxylamine by atmospheric oxygen,[164,165] in the reduction of nitric oxide by hydrogen,[142,166] and in the photochemical reduction of nitro-compounds[167] has been demonstrated. The catalytic activity of MPhc in the electrochemical oxidation of hydrazine has also been established.[168,169] Depending on the nature of the metal, the catalytic activity increases in the sequence NiPhc ≅ CuPhc < CoPhc < FePhc.

## IV. CATALYSTS OF ISOMERISATION AND POLYMERISATION REACTIONS

Studies have shown[170–180] that cobalt-porphyrins are unique regulators of the degree of polymerisation of acrylates and it has been established that CoP catalyses the reaction involving chain transfer to the monomer:

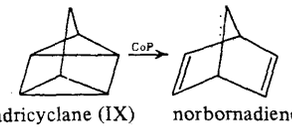



(24)

The degree of polymerisation is regulated by the simple alteration of the concentration of the CoP introduced into the initial monomer. The efficiency of the catalyst in the reaction involving chain transfer to the monomer can be inferred from the following example:[176] the polymerisation of methyl methacrylate in bulk at 233 K and at an initiator (azobisisobutyronitrile) concentration of $2 \times 10^{-2}$ M without added regulator yielded a polymer with an average degree of polymerisation of $4 \times 10^3$. Under the same conditions but with addition of $6 \times 10^{-4}$ M CoHaeP to the initial mixture, the average degree of polymerisation fell to 8.1.

The catalytic activity in the chain transfer to the monomer is shown only by the cobalt complexes of the porphyrins proper. The Ni, Cu, Zn, Cr, Mn, Pd, and TiO complexes as well as MPhc inhibit the polymerisation of methyl methacrylate.[177] The nature of the side groups in the porphyrins is relatively insignificant. The phenomenon described is observed in the polymerisation of acrylates and styrene. Catalytic chain transfer to the monomer with the aid of MP has not been observed for other monomers. It has been established[180] that the mechanism of the chain transfer to the monomer involves the transfer of a hydrogen atom from the methyl group of the growing chain to the cobalt atom of the catalyst with its subsequent transfer to the monomer. Catalysts grafted to a heterogeneous carrier have been synthesised and investigated in order to achieve the practical realisation of the method described above for the regulation of the degree of polymerisation of acrylates.[178]

Certain MP are able to catalyse the dark and photochemical isomerisation of unsaturated compounds. For example, the catalytic activity of CoP in the isomerisation of quadricyclane to norbornadiene has been established:[181–183]

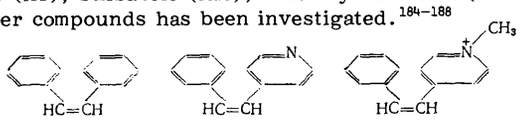



quadricyclane (IX) norbornadiene (X) (25)

In conformity with the Woodward–Hoffman rules, this reaction is symmetry-prohibited and therefore proceeds at a very low rate. The complexes of $H_2TPhPo$ with Co(II) and Co(III) increase sharply the rate of isomerisation probably via the extracoordination of quadricyclane. The catalytic activity of Co(III)TPhPo is greater by two orders of magnitude than that of Co(II)TPhPo. The reaction rate depends strongly on the nature of the organic solvent.

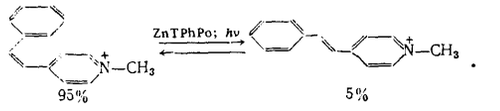
## V. CATALYSIS OF PHOTOCHEMICAL AND PHOTOELECTROCHEMICAL REACTIONS

The metalloporphyrin-sensitised photoisomerisation of stilbene (XI), stilbazole (XII), *N*-methylstilbazole (XIII), and other compounds has been investigated.[184–188]




*cis*-stilbene (X) *cis*-stilbazole (XII) *cis*-*N*-methyl-4(β-styryl)-pyridinium (XIII)

It has been shown that under photostationary conditions the N-methyl-4-(β-styryl)pyridinium salt forms an equilibrium mixture of *cis*- and *trans*-isomers enriched in the *cis*-isomer:




(26)

It must be emphasised that, in the absence of metalloporphyrins [ZnTPhPo or Sn(Cl)TPhPo], the *cis*- and *trans*-isomers of *N*-methyl-4-(β-styryl)-pyridinium are completely stable in the dark. The authors[188] concluded that the isomerisation proceeds via electron transfer from the photoexcited MTPhPo molecule to the substrate.

The photoisomerisation of stilbene, stilbazole, and related compounds is observed in the presence of zinc and magnesium[185,187] as well as platinum and palladium[184] complexes of the porphyrins. Under photostationary conditions, the *trans*-isomers of the compounds accumulate. Thus, in the isomerisation of stilbene the content of the *trans*-isomer can reach 85%; stilbazole is converted under photostationary conditions into the *trans*-isomer in 95–99% yield. It was of interest that, in the presence of the zinc complex of aetioporphyrin (ZnAePo), stilbene undergoes *cis–trans* isomerisation with a quantum yield of 0.01, while the analogous reactions of stilbazole and its derivatives have a quantum yield up to 6.6. This means that the absorption of one quantum of light by the ZnAePo molecule leads to the conversion on average of 6.6 *cis*-stilbazole molecules into *trans*-stilbazole. In the discussion of the reaction mechanism, the authors[185] suggested the formation of an extracomplex of stilbazole with MP in an excited triplet state.

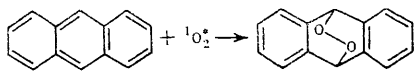
The unique photophysical and photochemical properties of porphyrins have been used in the development of new light-sensitive materials for three-dimensional phase holography. The proposed[189,190] light-sensitive materials consist of a polymer matrix in which substituted anthracene and a porphyrin sensitiser, for example, mesoporphyrin ($H_2MPo$) are dispersed. Before recording the hologram, the polymer matrix is saturated with oxygen at a pressure of 80–140 atm. Next, the holographic image is recorded in the usual way. On irradiation with light, porphyrin passes to an excited state, initially singlet and then triplet. The porphyrin in the excited triplet state undergoes a bimolecular reaction with molecular oxygen and leads to the transition of the latter from the ground triplet state to the excited singlet state:

$$H_2P + h\nu \rightarrow {}^1H_2P^* \; ; \qquad (27)$$

$$^1H_2P^* \rightarrow {}^3H_2P^* \; ; \qquad (28)$$

$$^3H_2P^* + {}^3O_2 \rightarrow H_2P + {}^1O_2^* . \quad (29)$$

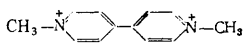
Singlet oxygen is a powerful oxidant which oxidises anthracene, the reaction being controlled by the rate of diffusion:



(30)

The endoperoxide formed has a refractive index which differs from the initial anthracene. Thus, when a hologram is recorded, regions with different refractive indices are generated in the polymer matrix. The image is then fixed. For this purpose, the hologram is kept in the dark at normal pressure in order to remove the oxygen dissolved in the matrix. In order to reproduce the holographic image, visible light is passed through the hologram. The interference pattern, giving rise to the effect of a three-dimensional image, arises as a result of the different phase shifts in the electromagnetic vibrations of the visible light which has passed through regions with different refractive indices.

One of the possible practical applications of porphyrins in the future may be catalysis of the photochemical decomposition of water in order to utilise solar energy. Comparatively recently, Shilov[191] showed that irradiation of a system comprising ethylenediaminetetra-acetic acid, methylviologen ($MV^{2+}$) (XIV) (an acridine dye), and a colloidal solution of platinum results in the evolution of hydrogen:



methylviologen (XIV) .

The acridine dyes used in the first studies in order to sensitise the photochemical reduction of water utilise only a limited proportion of the sun's rays. Porphyrins, whose absorption spectra cover an appreciable proportion of the spectrum of the sunlight reaching the surface of the Earth, are of great interest in this respect. For example, $H_2$TPhPo can absorb 46% of the energy of the sun's rays, while ZnTPhPo and PdTPhPo can absorb 40 and 25% respectively.[192] One must bear in mind that many $H_2P$ and MP exhibit a very high photochemical stability.

Studies have shown that the metal complexes of phthalocyanine and its derivatives are relatively ineffective sensitisers of the photochemical decomposition of water.[193–195] This can be accounted for by the low energy level of the triplet excited states of MPhc. The porphyrin complexes, particularly those which have positively charged functional groups, for example, the complexes of tetra(*N*-methylpyridyl)-porphin ($MTMePyPo^{4+}$) are more promising. The quantum yield in the evolution of hydrogen on reduction of water in the $ZnTMePyPo^{4+}$/EDTA/$MV^{2+}$/Pt system reaches 0.3.[196–200]

The sequence of reactions in the photochemical reduction of water can be represented as follows:

$$MP \xrightarrow{h\nu} MP^* ; \quad (31)$$

$$MP^* + MV^{2+} \rightarrow MP^+ + MV^+ ; \quad (32)$$

$$MV^+ + H_2O \xrightarrow{Pt} MV^{2+} + {}^1/_2H_2 + OH^- ; \quad (33)$$

$$MP^+ + EDTA \rightarrow MP + EDTA^+ . \quad (34)$$

The first stage involves the photoexcitation of the metalloporphyrin, which then reduces methylviologen. When colloidal platinum is used as the cocatalyst, the accumulation in solution of the reduced form of methylviologen is a sufficient condition for the evolution of hydrogen from water. Without methylviologen, the quantum yield in the photochemical reduction of water on a MP is $10^{-4}$–$10^{-3}$.[198,200,201]

Methylviologen is an effective quenching agent for the singlet and triplet states of porphyrins. However, one must bear in mind that $MV^+$ can recombine with the oxidised form of the sensitiser:

$$MV^+ + MP^+ \rightarrow MV^{2+} + MP . \quad (35)$$

Thus the yield of hydrogen in the reduction of water depends on the ratio of the rates of the competing reactions (33) and (35).

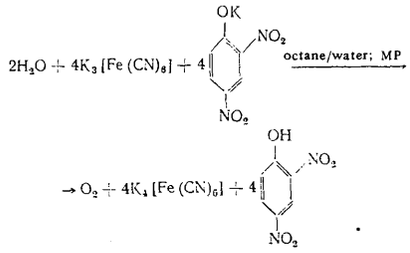
The rate of recombination can be diminished, firstly, by employing a sensitiser in the triplet excited state as the reductant in reaction (32). The recombination reaction is then spin-prohibited, since the reverse electron transfer from $MV^+$ to $MP^+$ requires a change in the spin state of the system:

$$^3(MP^+ \ldots MV^+) \rightarrow {}^1MP + {}^1MV^{2+} .$$

Secondly, in order to suppress the recombination process, it is useful to employ positively charged sensitisers, for example, complexes of tetra-(*N*-methylpyridyl)porphin. In this case the electrostatic repulsion of the reactants $MTMePyPo^{5+}$ and $MV^+$ prevents their recombination. The rate of reduction of methylviologen [reaction (32)] diminishes at the same time. However, experiment has shown that the introduction of positively charged functional groups into the molecule of the porphyrin sensitiser sharply increases the yield of hydrogen.[196–200] When negatively charged sensitisers are used, for example, the complexes $H_2TPhPo(SO_3^-)_4$, the quantum yield in the photogeneration of hydrogen does not exceed several tenths per cent.[199] Thirdly, in order to eliminate reaction (35) and the regeneration of the initial form of the sensitiser, the so-called sacrificial donors (EDTA, cysteine, amines) are used. The role of these compounds is to reduce the oxidised sensitiser [reaction (34)]. The oxidised donor, for example $EDTA^+$, does not react with $MV^+$ and is irreversibly consumed in the reduction of water. Hydroquinone, which can be, in principle, regenerated in the photochemical oxidation of water to molecular oxygen, has been proposed as a reductant of this kind.[202]

Mainly zinc complexes have been used in the study of the porphyrin sensitisers of the photochemical reduction of water. However, it is known that magnesium,[202,203] tin,[204] ruthenium,[205] and metal-free haematoporphyrin[337] exhibit a high activity in this process. It has been shown[202,203,206–209] that, together with water-soluble sensitisers, complexes of neutral porphyrins dispersed in micelles can be used in the reduction of water. A review of studies on the photodissociation of water sensitised by porphyrins has been published.[192]

The systems described can be used, in principle, to obtain hydrogen subject to the obligatory condition that the process can be combined with the photochemical oxidation of water, i.e. the reaction involving the irreversible consumption of the sacrificial donor is eliminated. Studies[213,214] where it has been shown that metalloporphyrins, for example, chlorophyll, can sensitise the photochemical oxidation of water to oxygen in two-phase systems of the type of water–octane, are interesting in this respect. For the reaction to be carried out, it is essential that oxidants [potassium hexacyanoferrate(III), etc.] and weak proton acceptors, for example, potassium 2,4-dinitrophenoxide, are present:




(36)

The oxidation of water in these systems involves the photoexcitation of the MP with its subsequent oxidation by a weak oxidant:

$$MP^{*}+[Fe(CN)_6]^{3-}\rightarrow MP^{+}+[Fe(CN)_6]^{4-}. \quad (37)$$

The products of reaction (37) do not recombine, because the reactants are in different phases: MP is in octane while the reduced form of the oxidant is in water. Next, water is oxidised by the metalloporphyrin radical-cation. Together with chlorophyll, the iron complex of coproporphyrin exhibits a fairly high photocatalytic activity in this reaction. This is extremely remarkable, because FeP do not have long-lived triplet states.

The photocatalytic systems described above suffer from two significant disadvantages. Firstly, they are complex and, secondly, the water photochemical oxidation and reduction reactions cannot as yet be combined in a single process. The comparatively simple photoelectrochemical method for the decomposition of water into hydrogen and oxygen is attractive in this respect.[216,221]

It has been established[215,218–221] that, when the electrochemical cell $Pt|(MgChl\alpha.2H_2O)_n|H_2O|Pt$ is irradiated with red light, a photocurrent flows through it and water is cleaved into hydrogen and oxygen. The electrophotodissociation of water can be described as follows:

$$Pt|(MgChl\alpha.2H_2O)_n(\text{photocathode}):\ 2H_2O + 2e^- \rightarrow H_2 + 2OH^-; \quad (38)$$

$$Pt(\text{photoanode}):\ 2H_2O \rightarrow 4H^+ + O_2\ 4e^-. \quad (39)$$

The photoelectrochemical reduction of water apparently takes place on chlorophyll *a* dihydrate dimers $[MgChl\alpha.2H_2O]_2$. The quantum yield of hydrogen on irradiation of the above cell with light at a wavelength of 735 nm is 0.88%.[221] A photoelectrolytic apparatus based on a platinised polycrystalline chlorophyll *a* dihydrate deposited on a platinised metallic support has been described in a patent.[219] This apparatus makes it possible to photodissociate water with a quantum yield up to 0.2. It has been shown[217] that polycrystalline chlorophyll *a* dihydrate can be used as the photoanode in the electrochemical cell. However, the activity of such anodes is greatly inferior to that of the platinum anode.

The photoelectrochemical oxidation-reduction reactions catalysed by $H_2P$ and MP have been widely investigated in order to devise converters of solar energy into electrical energy.[222–236] The pigmented electrode serves as the photocathode in almost all photoelectrochemical cells of the type electrode |MP (or $H_2P$)|electrolyte|electrode. The charge carriers are generated in most cases at the MP|electrolyte interface and in some cases at the electrode|MP interface. The mechanism of the generation of the photocurrent as a rule involves the formation of an excited triplet state of the sensitiser, the migration of the triplet exciton state to the MP|electrolyte interface, the generation of charges on this interface as a result of electron transfer from the photoexcited sensitiser to $H^+$, $O_2$, or to an oxidant specially introduced into the electrolyte, and finally the migration of the charges to the current measuring devices. In agreement with this mechanism, the photocurrent flowing through photoelectrochemical cells increases sharply when oxidants such as methylviologen,[224,233] potassium hexacyanoferrate-(III),[222] etc. are introduced into the electrolyte. An appreciable increase of the photocurrent quantum yield is observed when the thickness of the pigment layer is decreased to approximately 3 nm.[222,223,233] Ilatovskii[223] states that, for a greater thickness of the porphyrin sensitiser layer, the exciton states formed in the bulk of the film cannot reach the MP|electrolyte interface. Furthermore, with increase of the thickness of the pigmented film, its ohmic resistance and the probability of the recombination of the charge carriers also increase.

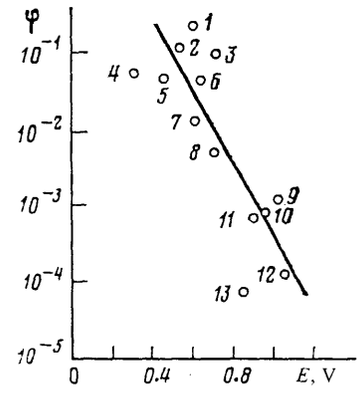



**Figure 2.** Dependence of the photocurrent quantum yields $\phi$ of the cells $Al|MP|[Fe(CN)_6]^{3-}, [Fe(CN)_6]^{4-}|Pt$ on the first oxidation potentials of the porphyrins:[236] *1*) MgPo; *2*) MgTPhPo; *3*) ZnPo; *4*) ZnTPhIBCh; *5*) CdTPhPo; *6*) CdTPhPo; *7*) ZnTPhCh; *8*) ZnTPhPo; *9*) CdTPhPo; *10*) $H_2$TPhPo; *11*) CuTPhPo; *12*) CoTPhPo; *13*) PtTPhPo ($H_2$TPhIBCh = tetraphenylisobacteriochlorin; $H_2$TPhCh = tetraphenylchlorin).

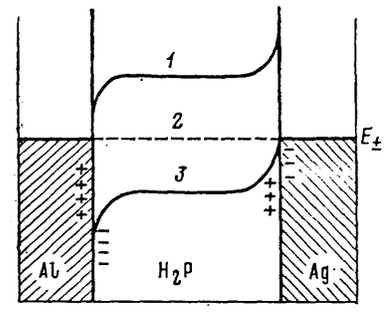



**Figure 3.** Schematic illustration of the energy levels in the cell $Al|H_2P|Ag$:[266] *1*) conductivity level; *2*) Fermi level; *3*) valence level.

The photocurrent quantum yield depends significantly on the nature of the porphyrin sensitiser and in the first place on its reducing properties. The photoelectrochemical

properties of 30 porphyrins and metalloporphyrins have been investigated[236] with the aid of the cell Al|porphyrin|[(Fe.$(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$|Pt and it has been established (Fig.2) that the photocurrent quantum yield increases with decrease of the oxidation potential of the porphyrin sensitiser. The most active sensitisers MgPo, ZnTPhPo, and ZnPo ensure a photocurrent quantum yield up to 0.2. Certain MPhc exhibit a high electrochemical activity. Thin-film converters of solar energy, ensuring a photocurrent quantum yield up to 0.15 and an energy efficiency up to 2% have been developed on their basis.[222,223] The photoelectrochemical activity of complexes of tetra(*N*-methylpyridyl)porphin,[225] tetra(*N*-stearylpyridyl)porphin,[226,227] chlorophyll,[216–221,232] and other porphyrins[236] has also been demonstrated.

## VI. SEMICONDUCTORS AND PHOTOCONDUCTORS

Porphyrins possess semiconducting properties and their electrical and photoelectrical properties have been investigated vigorously.[222–224,236,240–292] They are known to possess intrinsic hole conductivity.[212,225,256,279,283] Sandwich cells with two different electrodes, for example Al|$H_2$P(MP)|Ag, have voltage-current characteristics typical for barrier diodes. The blocking layer in the cells is formed as a consequence of the flow of electrons from an aluminium or another electrode with a low electron work function to the porphyrin. This results in the formation of a zone depleted in charge carriers. Its size is 1.5–3 nm depending on the nature of the $H_2$P. At the $H_2$P|Ag interface, electrons pass from the porphyrin cell to the electrode (Fig.3). The resulting distortion in the valence and conductivity levels ensures the migration of the charge carriers photogenerated in the porphyrin film to the electrodes: positive ones to the silver electrode and negative ones to the aluminium electrode.

Porphyrins have a molecular crystal lattice and a low intermolecular interaction energy. The absorption of light results in their intramolecular excitation. The high-lying conductivity band is not then populated. The generation of charge carriers is achieved in the interaction of excited $H_2$P molecules with acceptor centres, which may consist of molecules of oxygen,[222,223,243,283] iodine,[283] or other doping additives. In the sandwich cells Al|$H_2$P|M (M = Ag, Pt, etc) charges are generated in the acceptor traps on the Al|$H_2$P interface, or more precisely on Al|$Al_2O_3$|$H_2$P.[225,256,285] In agreement with the hole character of the conductivity of $H_2$P and MP, the efficiency of the operation of the photocells is related directly to the ability of the porphyrins to be converted into radical-cations. Indeed, the photocurrent quantum yield increases with decrease of the oxidation potentials of the porphyrins.[225–283]

An evident way of increasing the concentration of charge carriers in semiconductors, namely by the introduction of doping admixtures, has only limited applicability to $H_2$P and MP. If the amount of admixture exceeds a specific level (~1%), the quality of the pigment films and hence the quality of the operation of the photocells are sharply impaired. A possible solution of this problem consists in the employment of MP with highly charged cations which contain donor or acceptor groups as the extraligands. For example, it has been established[241] that Al(Cl)Phc and In(Cl)Phc have specific conductances higher by 3–5 orders of magnitude than MgPhc and CuPhc, while their photosensitivity is higher by 2 orders of magnitude.

The specific conductances of $H_2$P and MP are usually in the range from $10^{-15}$ to $10^{-3}$ S m$^{-1}$. Studies[288–292] where it has been shown that, on application of a high pressure (h.p.) and on shear deformation (s.d.), the specific conductances of certain $H_2$P increase by 5–6 orders of magnitude are therefore of great interest. For example, the specific conductance of $H_2$TPhCo increases from $10^{-5}$ to 10–100 S m$^{-1}$ following the application of a pressure of 2–4 GPa and of s.d., while the activation energy for electrical conduction diminishes by a factor of ten.[288] The increase of electrical conductivity and the joint influence of high pressure and shear deformation depend on the nature of the side substituents in porphyrins,[289] on the nature of the central metal atom,[289,290] and on the size and structure of the conjugated system of π-bonds in polymeric phthalocyanines.[292] The increase of electrical conductivity following the application of high pressure and shear deformation has been explained[288–292] by the decrease of the potential barrier to the intermolecular jump of the charge carriers as a result of the mutual approach in space of neighbouring molecules in porphyrin crystals and the increase of the intermolecular overlap of their π orbitals.

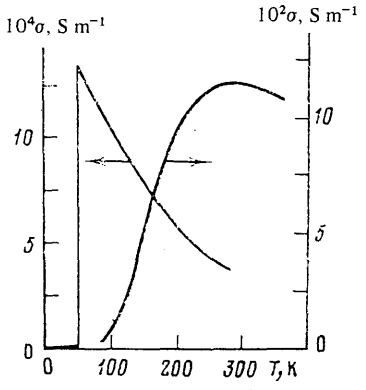



Figure 4. Temperature variation of the specific conductances of organic metals based on different porphyrin derivatives: *1*) NiOMTBPo$(I_3^-)_{0.35}$;[272] *2*) NiPhc$(I_3^-)_{0.33}$.[273]

Metal complexes of phthalocyanine and octamethyltetrabenzoporphin (MOMTBP) have been used[268–274,293] to synthesise organic metals of a new type. Compared with the initial MP, the organic metals obtained on their basis have specific conductances higher by 11–13 orders of magnitude. The increase of conductivity is achieved by treating crystailine MP with iodine vapour or solutions. Iodine plays the role of the oxidant and is converted into the anions $I_3^-$, which are arranged in chains within long narrow channels in the crystal lattice formed via stacks of parallel MP molecules. A fundamental feature of such crystals is the fractional positive charge per MP molecule. As a result, neutral and positively charged MP species alternate in the stack. There is also a possibility of structures with alternation of porphyrin mono- and di-cations. It is of interest that the electrical properties of $MP_n^{m+}(I_3^-)_m$ crystals depend very little on the average fractional positive charge per MP species. The organic metals based on MPhc exhibit metallic electrical conductivity, i.e. their conductivity diminishes with increase of temperature. The temperature dependence of the electrical conductivity of partly oxidised NiOMTBP is represented by a curve with a maximum at 260–330 K (Fig.4).

In conclusion, one should note that materials with a high electrical conductivity can apparently be obtained not only from partly oxidised but also from partly reduced MP.[294]

## VII. ELECTROCHROMIC MATERIALS

By splitting off or combining with one or several electrons, $H_2P$ readily form radical-ion species.[295] The porphyrin radical-ions are very stable and can be generated by chemical or electrochemical methods. It is significant that different radical-ion species have different spectroscopic characteristics. The electrochemical method for the generation of porphyrin radical-ions deposited on optically transparent electrodes, for example, $SnO_2$ or $In_2O_3$ electrodes, is of special interest from the practical point of view. The colour of such electrodes is determined by the applied electrical potential and this can be used in a wide variety of electrochromic devices. The phthalocyanine complexes of Co, Mo, Fe, Mn, Zn, and the lanthanides possess electrochromic properties.[296–299]

Compared with liquid crystals, which are used widely as electrochromic materials, MP have the advantage that they can repeatedly change their colour depending on the sign and magnitude of the polarising potential. The diphthalocyanine complexes of the lanthanides are of particular interest in this respect. For example, as the electrical potential varies, the diphthalocyanine complex of lutetium changes colour five times;[299] its colour can be red, green, blue, and violet. The electrochromic materials based on MP are very durable in use, permitting not less than 100000 colour change cycles.[298]

## VIII. PIGMENTS, DYES, AND FOOD DYES

Tens of thousands of tonnes of MPhc are produced annually as pigments and dyes in industrially developed countries.[268] The interest in these dyes is due to their high photostability, chemical and migrational stability, and the purity of colour tones. Hundreds of publications, mainly patents, have been devoted to phthalocyanine pigments and dyes. Porphyrins proper can also be used as technical dyes. They have all the advantages of the phthalocyanine dyes and have a very wide colour range. However, the practical use of porphyrin pigments and dyes is possible only when their cost is sharply reduced.

Certain readily available porphyrins have found applications as food dyes.[300,301] Thus chlorophylls (a + b), their copper analogues, and the copper complexes of phaeophorbide (a + b) are permitted food colourants in almost all the major foreign countries. As early as 1926, about 20 tonnes of chlorophyll were processed in the U.S.A. for the colouring of food products.[301]

It has been suggested[300] that the cobalt complex of the disodium salt of haematoporphyrin be used to impart a red colour to sausage products. Sodium nitrate is used at present for this purpose. The addition of $(3–5) \times 10^{-3}$ wt.% of the cobalt complex makes it possible to reduce greatly the amount of nitrite introduced into the sausage meat and to eliminate the appearance of residual nitrite and nitrosamines.

## IX. ENRICHMENT OF RADIOISOTOPES

Phthalocyanines are used to synthesise and enrich radioisotopes by the Szilard–Chalmers method,[302–325] which consists of bombarding MPhc specimens with thermal neutrons. Isotopes with higher mass numbers are formed as a result of neutron capture by the nuclei of the coordinated metals. The nuclear reaction is terminated by the emission of a $\gamma$-quantum. Recoil results in the decomposition of the MPhc and the liberated isotope forms a new chemical compound. For the successful application of the Szilard–Chalmers method, the initial coordination compound must have high chemical, thermal, and radiation stabilities. Metalloporphyrins satisfy these requirements. Phthalocyanine complexes have been used to obtain Cu, Zn,[99] Co,[303,306] Ro,[305] and lanthanide[315] isotopes. The yields of radioisotopes obtained by the Szilard–Chalmers method using MPhc are as a rule high. For example the yields of 13 lanthanide isotopes were between 60 and 90%.[315] The enrichment factors were in the range $10^2–10^3$.[99,315]

Table 2. Porphyrins as analytical reagents

| Element to be determined | Analytical reagent | Analytical method | c, M | Refs. |
|---|---|---|---|---|
| Cu(II) | $H_2TPhPo(SO_3H)_3$ | SPPM | $1\cdot10^{-7}–1\cdot10^{-6}$ | [317, 318, 342] |
| | $H_2TPhPo(SO_3H)_4$ | F | $10^{-7}–10^{-6}$ | [319] |
| | " | E | | [326] |
| | $H_2TPhPo$ | SPPM | $7\cdot10^{-8}–2.5\cdot10^{-6}$ | [323] |
| | $MTPhPo(COOH)_4$ | " | $10^{-7}–10^{-6}$ | [328] |
| | $MTPhPo(SO_3H)_4$ (M = Cd, Hg, Pb*) | | | |
| | $H_2OAePo$ | E | $5\cdot10^{-5}$ | [341] |
| | $H_2T(3\text{-MePy})Po$ | SPPM | $10^{-7}–10^{-6}$ | [330, 347] |
| | $H_2T(4\text{-MePy})Po$ | " | $10^{-7}–10^{-6}$ | [318, 321, 324] |
| | $H_2T(4\text{-MePy})Po$ | SPPM-CIER | $10^{-8}–10^{-7}$ | [335, 344] |
| | " | AD-SPPM | $10^{-7}$ | [327] |
| | " | E | $10^{-7}$ | [326, 346] |
| | $PbT(4\text{-MePy})Po$ | TLS | $10^{-6}$ | [346] |
| | Haemoglobin | P | | [343] |
| Zn(II) | $H_2TPhPo$ | SPPM | $6\cdot10^{-6}–3\cdot10^{-5}$ | [316] |
| | $H_2T(3\text{-MePy})Po$ | " | $1.3\cdot10^{-7}–2.5\cdot10^{-6}$ | [332] |
| | $H_2TPhPo(4\text{-}NMe_3)_4$ | P | | [339] |
| Cd(II) | $H_2TPhPo(SO_3H)_4$ | SPPM | $10^{-7}–10^{-6}$ | [325] |
| | $H_2TPhPo(COOH)_4$ | | | |
| | $H_2T(3\text{-MePy})Po$ and | SPPM and | $10^{-6}$ | [330] |
| | $H_2T(4\text{-MePy})Po$ | AD-SPPM | $10^{-7}$ | |
| | $H_2TPhPo(SO_3H)_4$ | C | $10^{-9}$ | [345] |
| Hg(II) | $H_2TPhPo(SO_3H)_4$ | C | $10^{-9}–10^{-8}$ | [334] |
| Mn(II) | $CdTPhPo(COOH)_4$ | SPPM | $5\cdot10^{-7}–1\cdot10^{-5}$ | [331] |
| Mg(II) | $H_2T(4\text{-MePy})Po$ | F | $10^{-6}$ | [320] |
| Ce(IV) | $CaPhc(SO_3H)_4$ | SPPM | $7\cdot10^{-7}–3.2\cdot10^{-5}$ | [340] |
| | $H_2Phc(SO_3H)_4$ | " | $7\cdot10^{-7}–1.3\cdot10^{-5}$ | |
| | $NiPhc(SO_3H)_4$ | " | $7\cdot10^{-7}–1.3\cdot10^{-5}$ | |
| As(III) | $H_2Phc(SO_3H)_4$ | SPPM-INCE | $2.7\cdot10^{-6}–2.7\cdot10^{-5}$ | [340] |
| | $NiPhc(SO_3H)_4$ | | | |
| | $CaPhc(SO_3H)_4$ | | | |

Notation. SPPM = spectrophotometry; SPPM-CIER = spectrophotometry with preliminary concentration on ion-exchange resins; AD-SPPM = analogue derivative spectrophotometry; TLS = pulsed laser thermal lens spectrophotometry; SPPM-INCE = indirect spectrophotometric determination using Ce(IV); F = fluorimetry; P = polarography; E = extraction–photometric method; C = catalytic method; c = concentration of the element to be determined.

*The metalloporphyrins indicated can be used also to determine Zn, Co, and Mn.

## X. ANALYTICAL REAGENTS

Porphyrins have found applications as analytical reagents in the quantitative analysis of trace amounts of many metals (Table 2). Spectrophotometric analytical methods, based on the use of highly intense absorption bands in the electronic absorption spectra of porphyrins and metalloporphyrins, are mainly employed. The MP formation reactions are highly sensitive, which makes it possible to determine Cu, Zn, Cd, and other metals at concentrations in the range $10^{-7}$–$10^{-6}$ M with an error of 0.5–2%. Preliminary concentration of the salts on ion-exchange resins of the Chelex or Dowex types makes it possible to increase the sensitivity of the reaction by two orders of magnitude.

Selective highly sensitive methods for the catalytic determination of Cd and Hg, whereby it is possible to determine these metals at concentrations of $10^{-9}$ M, have been developed. The methods[334,345] are based on the catalytic acceleration of the coordination of $H_2P$ to Mn(II) salts in the presence of Cd(II) or Hg(II). Porphyrin analytical reagents have been employed to determine Cu and Zn in tap water, in high-purity chemical reagents, hair, etc.

## XI. OTHER APPLICATIONS

MP and MPhc are being studied vigorously as molecular oxygen transferring agents. The ability of the porphyrin complexes of Co, Fe, Mn, Ti, and Mo to fix oxygen reversibly under certain conditions has been demonstrated. These studies are in the main theoretical although patents on this subject have appeared in recent years.

Porphyrins are used in the therapy and early diagnosis of cancer. The ability of $H_2P$ to accumulate selectively in cancer cells is used in this case. On irradiation with u.v. light, the diseased regions exhibit a red fluorescence.

Porphyrins manifest radioprotecting and radiosensitising properties and, depending on the concentration, they can intensify the radiation damge of a living organism and biological objects or can exhibit the opposite effect. Methods have been developed for the local decomposition of cancer cells based on the radiosensitising activity of $H_2P$ and on their ability to accumulate selectively in cancer tumours.

Among other applications, mention may also be made of applications of porphyrins in fields such as the determination of the quality of meat products and their use as inhibitors of the burning of plastics, as antistatic agents, and even as deodorants and stimulants of hair growth.

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# Reaction Chromato-mass Spectrometry

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The principles of the highly effective reaction chromato-mass-spectrometric method, based on the use of chemical reactions of the test specimens directly in the reaction system of a chromato-mass-spectrometer, are examined. The possibilities of the method in the determination of the structures of organic compounds and in the study of the mechanisms of dissociative ionisation, heterogeneous-catalytic reactions, and high-molecular-weight compounds are demonstrated.
The bibliography includes 52 references.

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## I. INTRODUCTION

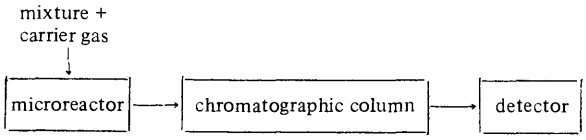
Preliminary chemical transformation of the test specimens is a common methodological procedure in the mass-spectrometric study of organic compounds. Various chemical methods, mainly derivatisation methods, are used in mass spectrometry to increase the volatility and the thermal and catalytic stabilities of the substances analysed, to improve the chromatographic characteristics (in chromato-mass-spectrometric investigations), to obtain additional information about the structure from the mass spectra of the reaction products, and to increase the sensitivity of the method in selective ionic detection.[1,2] The use of degradation methods (hydrolysis, pyrolysis) is extremely effective in mass-spectrometric research.[3,4] The majority of the known chemical modification methods are based on the use of reactions in solution. In such reactions, carried out in separate experiments, much labour and time must be expended on the isolation and separation of the products. In many instances comparatively large (microgramme) amounts of the test specimen are used in the chemical reactions. However, a much more convenient chemical transformation procedure involves gas-phase reactions in a microreaction system incorporated directly into the injection system of the mass spectrometer. Submicrogramme amounts of the test specimens, i.e. amounts sufficient for the mass-spectrometric analysis, can then be transformed. The most important advantage of this method is the possibility of carrying out the reactions directly in the course of the mass-spectrometric study. This creates a basis for the development of high-speed and highly effective research techniques whose possibilities are enhanced still further when chromato-mass spectrometry is employed. This method is called "reaction chromato-mass-spectrometry"[5] because it involves chemical reactions directly in the injection system of the chromato-mass spectrometer.

## II. PRINCIPLES OF REACTION CHROMATO-MASS SPECTROMETRY

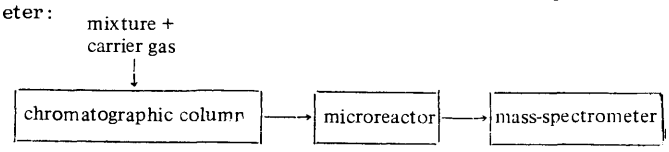
In reaction chromato-mass spectrometry (RCMS) the substances analysed or mixture components are modified chemically directly in the injection system of the chromato-mass spectrometer (in microreactors, in reactions on separating columns). This is done in order to alter the physicochemical properties of the substances analysed, in order to obtain from the mass spectra of the reaction product additional or new information about the structures of the starting materials, to investigate dissociative ionisation mechanisms, to study the modes and mechanisms of gas-phase reactions, etc. The familiar reaction gas-chromatographic (RGC) method may be regarded to some extent as a precursor of RCMS,[6] but distinctive features and advantages are characteristic of the RCMS method.

In the first place the value of the information about the structure which can be obtained by the above methods is not the same. Whereas RGC provides for the preparation of products with known chromatographic characteristics or the creation of simpler mixtures from complex mixtures by "subtracting" individual components, the RCMS method provides for specific modification of substances in order to obtain compounds whose mass spectra yield additional information about the structure of the starting materials. The most important advantage of the RCMS method is the possibility of synthesising compounds labelled with stable isotopes (in particular, deuterium) directly in the course of analysis, which is exceptionally promising in the study of the mechanisms of the dissociative ionisation of organic substances and reaction mechanisms. In RGC there is no such possibility.

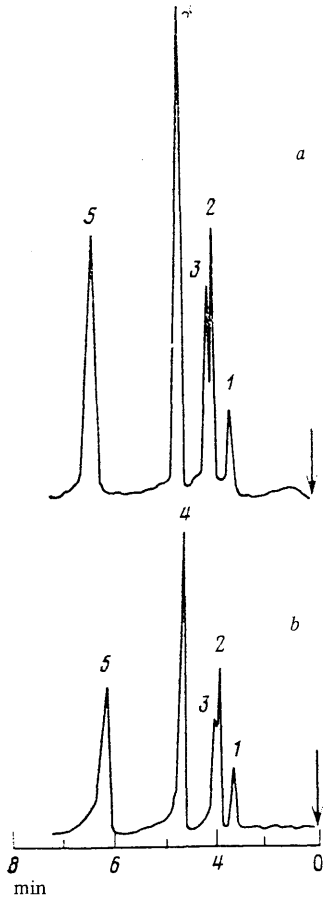
The microreaction system in RGC is usually placed before the separating chromatographic column:




Only when the subtraction method or the procedure is designed to increase the sensitivity of the analysis (if the detector is insensitive to the given component but is sensitive to its derivative) can the microreactor in RGC be placed between the column and the detector. In contrast to this, the microreaction system in RCMS is best located between the chromatographic column and the mass spectrometer:



The fundamental characteristic of this scheme is that each component eluted after chromatographic separation is subjected to chemical action. The chromatogram recorded under these conditions characterises the initial mixture (which ensures the possibility of a quantitative estimation of its composition), while the mass spectra correspond to the reaction products (which are used for structural assignments). This makes it possible to analyse separately even the isomeric compounds which give rise to identical structures on chemical modification and are naturally not susceptible to analysis by the RGC method.




Chromatogram of the initial mixture of alkenes (*a*) and the same mixture after passage through the hydrogenation microreactor placed between the column and the mass spectrometer (*b*): 1) 2,4,4-trimethylpent-1-ene; 2) oct-1-ene; 3) oct-2-ene; 4) non-1-ene; 5) dec-1-ene.[15]

In certain cases, for example, when it is necessary to decrease the polarity by means of a chemical reaction or to investigate the mechanism of a gas-phase process, the microreactor in the RCMS system can be usefully mounted before the separating column. The "subtraction microreactor" is positioned in the same way when there is a need to simplify the mixture for one reason or another.[7] Sometimes, especially in the analysis of individual substances, the separating column can be altogether disconnected and the microreactor is placed between the evaporator of the chromatograph and the mass-spectrometer.

As in RGC, in investigations by the RCMS method it is very important to select correctly the reactions which ensure the rapid, quantitative, and selective transformation of the substances analysed. Admittedly, a high selectivity is not always obligatory in relation to RCMS; it will be shown below that sometimes side reactions can assist in the determination of the structure.

In the RCMS method which provides for the gas-chromatographic injection of the test substances, gas-phase catalytic reactions are used for the chemical transformation of the compound. The amount of the catalyst required for the complete transformation of the compound depends to a large extent on the degree of its dispersion and on the necessary length of the reaction zone. In order to select the correct amount of the catalyst, the microreactor is placed before the chromatographic column and several experiments are performed varying the length of the catalyst bed and the amount of specimen injected. This also makes it possible to determine the process selectivity at different temperatures.

As stated above, the chemical reactions in RCMS can be achieved in microreactors, reaction columns, or directly in the separating column. A convenient wholly metallic microreactor for RCMS has been described.[8] The minimum number of valves whereby the substance in the stream of carrier gas can be passed either around the catalytic zone (by-pass) or through the catalyst bed are used in this reactor. The system is adequately miniaturised and can be placed within the chromatographic thermostat. The catalyst bed of the required height is placed in the microreactor cartridge between glass wool plugs.

The reaction columns employed in RCMS usually consist of metallic or glass tubes placed directly in the chromatograph thermostat. Such columns are filled with a catalytic packing or an active substance attached to a solid carrier, as in the preparation of packed analytic columns.

It is noteworthy that the RCMS method does not eliminate the need for the usual mass- or chromato-mass-spectrometric analysis of the initial compound. On the contrary, only a combined analysis of the mass spectra of the initial substances and their transformation products permits the most complete solution of structural-analytical problems.[9]

## III. INVESTIGATION OF THE STRUCTURES OF ORGANIC SUBSTANCES

### 1. Olefins

For the general case, in the study of the structures of olefins it is necessary to determine the structure of the carbon skeleton and the position and geometry of the double bond. Mass-spectrometry with ionisation by electron impact (EI) yields relatively little information in the solution of these problems owing to the preferential ionisation of unsaturated molecules at the double bond and the "migration" of the latter along the chain.[10,11] Many methods for the chemical "fixation" of double bonds, permitting the determination of their position and sometimes of their geometry from the mass spectra of the products, have been developed.[2,12] However, the majority of these methods are laborious, do not ensure the determination of the structure

of the carbon skeleton, and are unsuitable for the investigation of mixtures. New possibilities for the solution of these problems are provided by the RCMS.

The determination of the structure of the carbon skeleton of olefins is based on the fact that the mass spectra of paraffins, in contrast to those of unsaturated hydrocarbons, have many features from which one can infer the presence and character of branches in their carbon chains. Furthermore, the mass spectra of many alkanes are known and are contained in computer libraries and the structure of alkanes can therefore be sometimes established automatically. Olefins can be successfully hydrogenated in a microreactor placed in the injection system of a chromato-mass spectrometer when hydrogen is used as the carrier gas, serving simultaneously as a reactant. The efficiency of this procedure has been demonstrated in relation to the investigation of mixtures of α-olefins[13] and cyclohexenols.[14] However, the above method was used in these studies only to demonstrate the presence of the double bond and its other structural-analytical possibilities were not discussed. These questions were examined more thoroughly in other investigations.[5,15]

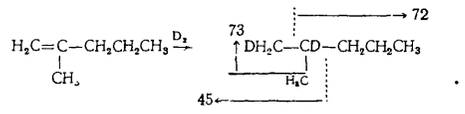
Olefins can be hydrogenated within the framework of the RCMS method using deposited platinum, palladium, or nickel catalysts. The 1-2% Pt/Chromaton and 1% Pd/porous glass catalysts, which ensure quantitative hydrogenation in the temperature range 50–250 °C without inducing undesirable reactions, in particular hydrogenolysis, have been employed for for such purposes.[5,15] The hydrogenation microreactor can be equally successfully placed after both packed and capillary columns and, when the amounts of the catalyst and the reaction temperature have been chosen correctly, an appreciable impairment of the chromatographic separation owing to the possible sorption of hydrocarbons on the catalyst is not observed (Figs. *a* and *b*). Using this method, the molecular weight of each component is established from the mass of the molecular ions ($M^+$) and the structure of the carbon skeleton can be determined from the mass spectra of the hydrogenation products. However, the problem of the determination of the position of the double bond remains. Its solution by the RCMS method can be achieved by the selective deuteriation of olefins at the double bond using deuterium as the carrier gas and the reactant. This approach has been studied in detail.[5,16]

**Table 1.** The isotope distribution (%) in the products of the deuteriation of n-octenes on the Pd/porous glass catalyst (100 °C).[16]

| Initial n-octene | [$D_n$]Octane | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $D_1$ | $D_2$ | $D_3$ | $D_4$ | $D_5$ | $D_6$ | $D_7$ | $D_8$ | $D_9$ |
| Oct-1-ene | 6 | 34 | 22 | 14 | 10 | 6 | 5 | 3 | — |
| Oct-2-ene | 4 | 20 | 15 | 15 | 12 | 8 | 8 | 6 | 6 |
| Oct-4-ene | 3 | 20 | 13 | 10 | 9 | 9 | 9 | 8 | 7 |

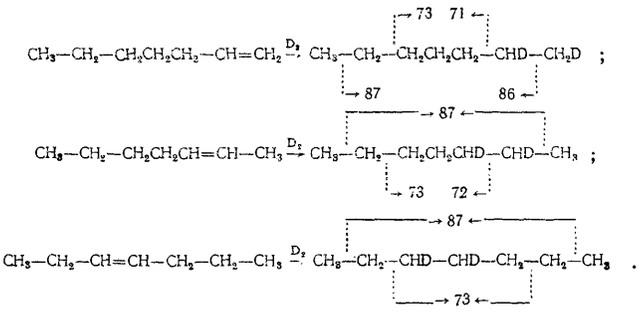
Heterogeneous hydrogenation catalysts based on transition metals are known[17] to ensure the selective deuteriation of olefins because they induce an intense exchange of the substrate hydrogen atoms for deuterium in both liquid-phase and gas-phase processes. However, this exchange proceeds more vigorously at elevated temperatures (>150 °C). It has been shown[5,16] that a decrease of the reaction temperature below 100 °C when the Pt/Chromaton and Pd/porous glass catalysts are used suppresses significantly the deuterium exchange. As an example, Table 1 presents the isotope composition of the products of the deuteriation of isomeric n-octenes. Evidently, in the case of an α-olefin deuterium exchange plays a less important role relative to deuteriation than in the case of olefins with inner double bonds. This finding can be used to differentiate olefins with terminal and inner positions of the double bond.

The deuterium exchange accompanying the addition of deuterium diminishes if the molecule contains a branch at the carbon atom involved in the double bond. This results in an increase of the fraction of vicinal dideuterioalkanes and the determination of the position of the deuterium label and hence of the position of the double bond in the olefin is thereby facilitated. For example, the spectrum of the product of the deuteriation of 2-methylpent-1-ene contains a doublet with equal peaks due to the fragment ions $[M-CH_3]^+$ ($m/z$ 73) and $[M-CH_2D]^+$ ($m/z$ 72) and also an intense peak of the ion with $m/z$ 45, which demonstrates unambiguously the position of the double bond:[5]




The next step in these studies involved the search for a metal complex catalyst which might be used in RCMS for selective deuteriation. Attention was turned to tris(triphenylphosphine)rhodium chloride (Wilkinson's catalyst, which is widely used for such purposes under homogeneous liquid-phase conditions.[18] However, the application of this catalyst in RCMS requires that it be made heterogeneous. Heterogeneous packing based on Wilkinson's catalyst had been obtained earlier by impregnating porous carriers with a solution of $(Ph_3P)_3RhCl$ in comparatively high-boiling liquids. These were used for the gas-phase hydrogenation and hydroformylation of lower olefins (ethylene and propene) at 25 °C.[19] However, this type of packing is unsuitable for RCMS, since the solvent evolved enters the mass spectrometer and creates a strong backgound. It was therefore suggested that the catalyst be converted into a heterogeneous form by depositing it, after dispersion in a stationary liquid phase (Carbowax 20 M), on Chromaton.[20] This catalytic system ensured the selective deuteriation of higher alkenes (up to $C_{12}$) in the gas phase at 50–80 °C under the conditions of heterogeneous catalysis. The column, filled with the catalyst on the carrier, was connected to a mass spectrometer and the substrate in a stream of $D_2$ was passed through it. It was shown[16,21] that the reaction column with an appropriate length ensures the quantitative deuteriation of mono- and di-substituted olefins with substituents attached at the double bond, mass-spectrometric analysis confirming the high isotopic purity of the vicinal dideuterioalkanes formed (>96%).

It is recommended that, for the mass-spectrometric determination of the position of the label in dideuterioalkanes, one should analyse the ions formed as a result of the elimination of the simplest alkyl radicals from molecular ions at the ends of the chain or at branching points. It is shown below how information about the mass numbers of the characteristic fragment ions from isomeric dideuterioheptanes can be used to determine the position of the double bond:



The method described can be employed also for the determination of the position of the double bond in branched alkenes. In the study of mixtures, the individual units of the apparatus are arranged in the following sequence:

separating column → reaction column → mass spectrometer.

It has been suggested that hydrogenation beyond the column, in the chromato-mass spectrometer, be used to determine the configuration of the centre in the 4-position in the stereoisomeric 4-vinyl-*trans*-4-decahydroquinolinols, obtained by the Norman reaction in the form of mixtures. The feasibility of this approach arises from the fact that the mass spectra of the ethyl analogues show intense peaks due to the ions $[M-C_2H_5]^+$, whose intensity depends on the configuration of the centre in the 4-position (the ease of the elimination of the substituent $C_2H_5$ is greater when it is in the axial position), whereas the formation of the ions $[M-CH=CH_2]^+$ is not characteristic of the vinyl analogues. It has been shown[22] that, when the 1–2% Pd/porous glass (150–200 °C) catalyst is used in chromatography in a stream of $H_2$, each component of the mixture of isomeric vinyl alcohols is converted quantitatively into the corresponding ethyl analogue with retention of configuration. The stereospecificity of the fragmentation on electron impact, of the same kind as that observed when the individual stereoisomers of 4-ethyl-substituted alcohols are passed through the direct injection system, is manifested in the mass spectra of the alcohols under these conditions.

Post-column hydrogenation can also be carried out in a tube made of a hydrogen-permeable alloy based on platinum or palladium.[23] After chromatography in a stream of hydrogen, hydrogenation takes place in this case on the walls of the tube and the hydrogen is removed by diffusion through the walls. Such a tube can serve as an effective interface between the chromatograph and the mass spectrometer.

## 2. Alicyclic Compounds

The necessity for the development of additional methods assisting in the determination of the structures of alicyclic compounds arose because their mass spectra frequently resemble the spectra of the isomeric olefins and do not always contain reliable features whereby one could distinguish condensed, bridged, spiran, and jointed systems and also to differentiate cyclopentane and cyclohexane structures.

Cyclic and olefinic structures can be distinguished by means of post-column hydrogenation, because only the mass spectra of the latter are then altered.[5] Further, this method is not applicable to cyclopropane compounds, which undergo ring opening under hydrogenation conditions with formation of aliphatic products. A special method was therefore developed for cyclopropane compounds which increases the diagnostic possibilities of the procedure.[24] The method is based on the use of the hydrogenolysis reaction, which takes place readily in the gas phase in the presence of the Pt/Chromaton, $PtO_2$, and Pd/porous glass catalysts.[25]

It has been shown that the hydrogenolysis of monoalkylcyclopropanes leads to the formation, under these conditions, of a mixture of compounds with branched (A) and linear (B) structures, which can be readily distinguished mass-spectrometrically:

$$\text{>}-R \xrightarrow{H_2} \underset{(A)}{(CH_3)_2CHR} + \underset{(B)}{CH_3CH_2CH_2R} ;$$

$$R = n\text{-}C_8H_{17},\ CH_2CH_2COOCH_3,\ CH_2CH_2COOC_2H_5 .$$

Regardless of the reaction temperature (50–200 °C) and the nature of the substituent R, the ratio of the products (A) and (B) is 94:6. This fact is important, because it allows the microreactor to be placed between the chromatographic column and the mass spectrometer. Indeed, although the measured mass spectrum constitutes the sum of the spectra of both products, it is largely determined by the structure (A). However, a new problem of the differentiation of the cyclopropane compounds and the isomeric branched olefins, which give rise to identical products on interaction with hydrogen, arises under these conditions:

$$\text{>}-R \xrightarrow{H_2} (CH_3)_2CHR \xleftarrow{H_2} H_2C{=}\underset{CH_3}{\underset{|}{C}}R .$$

It has been suggested that the problem be solved by employing deuterium as the carrier gas and the reactant, because deuteriation of cyclopropane and unsaturated compounds gives rise to products with different positions of the label, which can be readily determined from the fragment ions in the mass spectra:

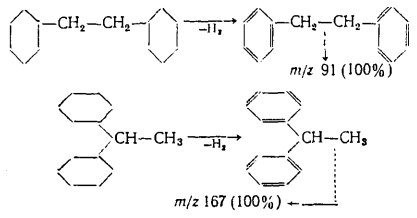
$$\text{>}-R \xrightarrow{D_2} DH_2C-\underset{CH_2D}{\underset{|}{CH}}-R ;$$

$$H_2C{=}\underset{CH_3}{\underset{|}{C}}-R \xrightarrow{D_2} DH_2C-\underset{CH_3}{\underset{|}{CD}}-R .$$

This method may prove to be exceptionally effective in the determination of the structures of cyclopropane derivatives of biological origin.[26]

It has been suggested that compounds containing five- and six-membered structures be investigated by means of the dehydrogenation reaction (Pt, C; 320 °C) in a microreactor positioned between the chromatographic column and the mass spectrometer.[27] In this case the process is carried out in a stream of carrier gas which consists of a mixture of 95% of helium and 5% of hydrogen. It has been shown for a large number of mono- and bi-cyclic hydrocarbons with known mass-spectrometric characteristics[28] that the cyclohexane derivatives contained in the mixtures, which do not contain quaternary carbon atoms, or compounds containing a six-membered ring which does not form part of the composition of bridged structures, are dehydrogenated with formation of the corresponding aromatic hydrocarbons. Five-membered cyclic derivatives do not react under these conditions. The number of six-membered rings in the initial molecule and also certain elements of the initial structures can be determined from the mass spectra of the aromatic hydrocarbons produced. The presence of intense $M^+$ peaks in the mass spectra of aromatic hydrocarbons permits a reliable determination of the molecular weight of the parent alicyclic compounds whose spectra do not contain the $M^+$ peaks. The characteristic decomposition of the aromatic hydrocarbons as a result of the benzil dissociation under electron impact makes it possible to detect branching at the

α-carbon atom of the alkyl substituent. In particular, 1,2- and 1,1-dicyclohexylethanes can be readily distinguished by this method:

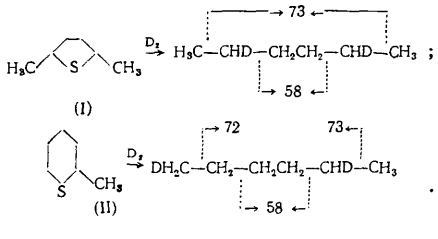



The structure of polycyclic hydrocarbons of the jointed type can also be established from the characteristic mass spectra of the dehydrogenation products.[29,30]

### 3. Cyclic Sulphides

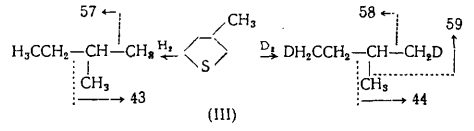
The RCMS method is used to study the structures of cyclic sulphides because EI mass spectrometry yields little information as regards the size of the heterocycle and the positions of its substituents. For a more reliable determination of the structures of monocyclic sulphides in mixtures, it has been suggested that the parallel hydro- and deuteriodesulphurisation of the mixture components in a microreactor placed between the chromatographic column and the mass spectrometer be used.[31] $Pd/Al_2O_3$ or Raney nickel could be used for the reaction, because both these catalysts give rise to effective hydrodesulphurisation in the presence of hydrogen at 150–250 °C. However, in the presence of deuterium, intense deuterium exchange takes place at these temperatures, while at lower temperatures $Pd/Al_2O_3$ becomes inactive. On the other hand, Raney nickel fixed on Chromaton by means of Apiezon is active also at 20–80 °C and at the same time ensures the selective formation of dideuteriohydrocarbons (the deuterium atoms are located at the carbon atoms which are linked to sulphur in the initial sulphides). The mass spectra measured under these conditions can be readily interpreted and make it possible to determine the position of the deuterium label and hence the size of the heterocycle. The positions of the substituents can be established in many cases on the basis of these spectra and also the spectra of the alkanes formed on hydrodesulphurisation.

It is easy to distinguish by this procedure, for example, 2,5-dimethylthiolan (I) and 2-methylthiane (II), whose mass spectra are similar. Although both compounds yield n-hexane on hydrodesulphurisation, the replacement of $H_2$ by $D_2$ leads to the formation of dideuteriohexanes with different positions of the label, which can be readily established mass-spectrometrically:[31]



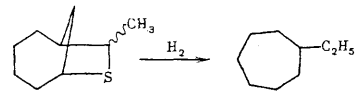

In the study of the structure of 3-methylthiolan (III), the position of the methyl substituent can be demonstrated already in the hydrodesulphurisation stage, since the recorded mass spectrum corresponds to 2-methylbutane.

The spectrum of the dideuteriohydrocarbon contains in its turn a doublet comprising peaks of equal size due to the ions $[M-CH_3]^+$ and $[M-CH_2D]^+$; this demonstrated unambiguously that the reaction product is 1,4-dideuteriomethylbutane and the initial sulphide therefore has the structure (III):

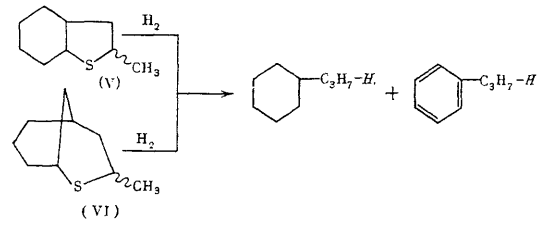



The employment of the deuteriodesulphurisation reaction in the study of polycyclic sulphides is pointless, since the position of the deuterium label in the naphthenic hydrocarbons formed cannot be determined mass-spectrometrically. Nevertheless, even simple hydrodesulphurisation can yield definite information about the structure of polycyclic sulphides. The qualitative composition of a mixture containing structural and geometrical isomers of methylthiabicyclononanes has been studied in this way.[32] The AP-56 catalyst, ensuring the quantitative hydrodesulphurisation of the test mixture at 300–315 °C, was then used. The desulphurisation microreactor was placed between a capillary column and the mass spectrometer. There was in this instance a risk that the separation of the eluted chromatographic zones would disappear even for small sorption effects of the catalyst. However, it was shown that, for an appropriate thickness of the catalyst bed, the impairment of the separation of the components, achieved with the aid of the capillary chromatographic column, is hardly detectable.

The results of the investigation confirmed the presence in the mixture of stereoisomeric 8-methyl-7-thiabicyclo[4.2.1]nonanes (IV), which gave rise to ethylcycloheptane on hydrodesulphurisation:




The mass spectra of the products of the hydrodesulphurisation of 8-methyl-7-thiabicyclo[4.3.0]nonanes (V), which are components of a mixture, consist of the spectra of the expected product (n-propylcyclohexane) and n-propylbenzene




Analogous mass spectra were recorded after the minor components had been passed through the catalytic zone. The structure of the isomeric 7-methyl-6-thiabicyclo[3.3.1]nonanes (VI) was proposed for such components.

Although the aromatisation of the cyclohexane hydrocarbons reduced the process selectivity and complicated the character of the mass spectra,[32] the latter are easy to interpret. Furthermore, this finding can be used to distinguish thiacyclanes with six-membered carbocycles

from the isomeric compounds with five- and seven-membered carbocycles. The characteristic nature of the mass spectra of aromatic hydrocarbons is also important, yielding additional information about the nature and positions of the substituents in the initial sulphides.

The results quoted by Mikaya et al.[32] are a good illustration of the fact that even those isomeric compounds which give rise to identical products in the reaction can be analysed separately by the RCMS method, which cannot be done by the RGC method.

## 4. Alcohols

Alcohols, especially aliphatic alcohols, are very important products of laboratory and industrial synthesis, frequently obtained in the form of mixtures. A wide variety of alicyclic alcohols (terpene and steroid alcohols) are isolated from biological objects. Thus the complexity of the mixture composition and the limited amount of the biological material available for study suggest that the chromato-mass-spectrometric method is most likely to be useful for their investigation. However, the mass spectra of the alcohols themselves yield insufficient information (or altogether fail to provide it) about their molecular weight and the nature and character of the carbon skeleton.[12] Derivatisation methods, based on liquid-phase reactions, are therefore very widely used for their investigations.[1,2] The RCMS method constitutes a good alternative to these procedures.

The combined RCMS method developed for the study of alcohols is based on the following gas-phase reactions.

1. The dehydrogenation reaction (catalyst—powdered copper; 320 °C)[33,34] carried out in a microreactor using helium as the carrier gas. Under these conditions, primary and secondary alcohols are quantitatively converted into aldehydes and ketones respectively, while tertiary alcohols remain unchanged. The mass spectra of the carbonyl compounds are characterised by the presence of $M^+$ peaks and also the peaks of the acyl ions $RCO^+$ and ions appearing as the result of the McLafferty rearrangement.

2. The reaction involving the exchange for deuterium of the enolysable hydrogen atoms in aldehydes and ketones formed on dehydrogenation of primary and secondary alcohols. This reaction takes place at 20–300 °C in a reaction column containing Chromaton on which dispersed KOD in a stationary SE-30 liquid phase is deposited.[35,36] The number of hydrogen atoms adjoining the carbonyl group exchanged for deuterium is determined from the shift of the $M^+$ peak, the peaks of the acyl ions, and the ions due to the McLafferty rearrangement.

3. The reaction involving the deoxygenation of alcohols to the corresponding hydrocarbons in the presence of a fused iron catalyst (300–320 °C).[37] It takes place in a microreactor in the presence of hydrogen, which serves at the same time as the carrier gas. The structure of the hydrocarbon is established from its mass spectrum by comparison with data in libraries of mass spectra or by analysing the characteristic decomposition under electron impact.

Various systems employed in the analysis of both individual alcohols (*A*–*C*) and their mixtures (*D*–*F*) have been developed on the basis of the reactions indicated:

*A*—dehydrogenation microreactor;
*B*—dehydrogenation microreactor → reaction column;
*C*—deoxygenation microreactor;
*D*—separating column → dehydrogenation microreactor;
*E*—separating column → dehydrogenation microreactor → reaction column;
*F*—separating column → deoxygenation microreactor.

All these systems can be placed in a thermostat of the chromatograph and connected to the inlet of the mass spectrometer.[38]

In the study of mixtures the analysis can be carried out in four stages. The chromatograms and mass spectra of the individual components of the initial mixture bypassing the reactor are recorded initially. The three subsequent stages of the analysis involve chromato-mass-spectrometric study using the *D*, *E*, and *F* systems. At each stage it is possible to obtain the relevant information about the structures of the individual elements of the alcohols investigated, which ultimately makes it possible to reproduce reliably the structure of the latter. Table 2 shows what information can be obtained from the mass spectra of aliphatic alcohols and their reaction products.

Table 2. Information about the structure of the alcohols obtained at different stages of their investigation by the RCMS method.[38]

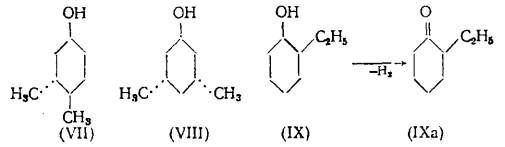
| Reaction employed | Product analysed | Information obtained |
|---|---|---|
| Without reaction (bypass) | initial alcohol | determination of approximate data on the molecular weight, the nature of the alcohol, and the position of the OH group |
| Dehydrogenation of alcohol | carbonyl compound | reliable determination of molecular weight; differentiation of primary, secondary, and tertiary alcohols and dialkyl ethers; determination of the position of the OH group; determination of approximate (sometimes accurate) data on the character of the branching at the carbon atoms in the α-position relative to the carbonyl group |
| Deuterium exchange involving dehydrogenation products | deuterium-labelled carbonyl compound | determination of the nature and character of the substitution at the carbon atoms in the α-position relative to the carbonyl group |
| Deoxygenation of alcohol | hydrocarbon | determination of the structure of the carbon skeleton of the alcohol |

It is noteworthy that in a number of instances there is no need to carry out all the stages of the investigation and it is sufficient to employ only some of them. Thus in the study of industrial alcohols, only the post-column dehydrogenation and pre-column deoxygenation were used.[39]

The RCMS method using the above reactions is very useful for the determination of the structures of alicyclic alcohols, whose mass spectra are relatively non-characteristic. The possibilities of the method have been demonstrated[40] in relation to mono- and bi-cyclic alcohols. In particular, it is possible to differentiate 3,4- and 3,5-dimethylcyclohexanols, compounds (VII) and (VIII) respectively, by this method and also to obtain information about their steric structures. After the deoxygenation, the mass spectra of *trans*-1,2-dimethyl- and *cis*-1,3-dimethyl-cyclohexanes respectively were recorded, which demonstrates a specific steric orientation of the $CH_3$ groups in the initial molecules.

When the *A* and *B* systems were used for the analysis of both alcohols, the mass spectra of ketones and their tetradeuterio-analogues were recorded respectively, which indicates the absence of substituents in the α-position relative to the OH groups. The fact that the spectrum of the ketone obtained from one alcohol [compound (VII)] contains peaks due to the ions $CH_3CH{=}CH\overset{+}{C}O$ (*m*/*z* 69) and

$CH_2=CHC\equiv\overset{+}{O}$ ($m/z$ 55), which shift when deuterium is used (the *C* system) to $m/z$ 70 and 56 respectively, while the spectrum of the ketone obtained from the other alcohol [compound (VIII)] contains only the peak of the first ion with $m/z$ 69 indicates the positions of the substituents in these cyclohexanols.




(VII) (VIII) (IX) (IXa)

Even simple dehydrogenation of 2-ethylcyclohexanol (IX) shows that it contains the $C_2H_5$ group in the α-position relative to the carbonyl group, since the maximum peak in the mass-spectrum of the ketone (IXa) is due to the $[M-C_2H_4]^+$ radical-cation, which appears as a result of the McLafferty rearrangement. This is also confirmed by the finding that only three hydrogen atoms in the ketone (IXa) are exchanged for deuterium.

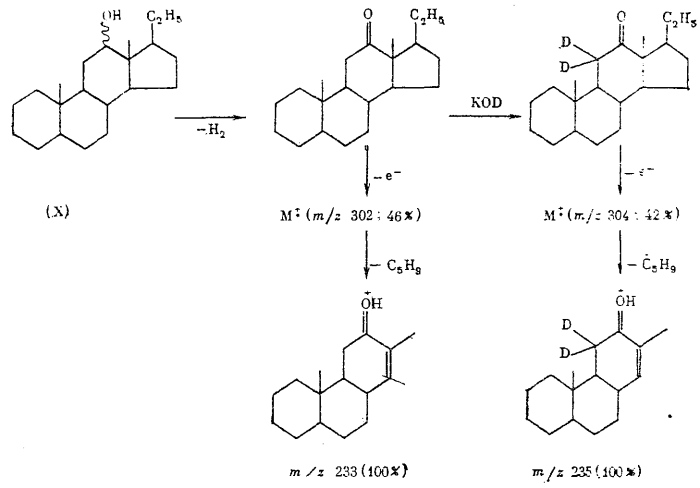
The problem of the mass-spectrometric determination of the position of the OH group is fairly acute in the case of steroid alcohols. The RCMS method gives rise to certain possibilities for the investigation of compounds of this type.[41]

**Table 3.** Composition of the products of the catalytic reactions of steroid alcohols (Cu, 320 °C, total conversion 100%).[41]

| Initial alcohol | Product (content in %) |
|---|---|
| 12α- and 12β-hydroxypregnanes (X) | 12-hydroxypregnane (100%) |
| 3β-Hydroxyandrostan-17-one | androstane-3,17-dione (100%) |
| 17β-Hydroxyandrostan-3-one | androstane-3,17-dione (100%) |
| Cholesterol | cholesta-3,5-diene (20%), cholesta-4,6-dien-3-one (70%), and cholest-4-en-3-one (10%) |
| 6-Methylcholesterol | 6-methylcholesta-3,5-diene (18%), 6-methylcholesta-4,6-diene-3-one (72%), and 6-methylcholest-4-en-3-one (10%) |
| 3β-Hydroxypregn-5-en-20-one | pregna-3,5-dien-20-one (15%), pregna-4,6-diene-3,20-dione (78%), and preg-4-ene-3,20-dione (7%) |

Table 3 presents the results of the investigation of individual steroid alcohols by the RCMS method using the dehydrogenation microreactor → separating column system. In all cases the alcohols react quantitatively. Saturated alcohols (hydroxypregnanes and hydroxyandrostanones) were only dehydrogenated under these conditions with formation of the corresponding ketones. On the other hand, mixtures were obtained from unsaturated alcohols (cholesterol, 6-methylcholesterol, 3β-hydroxypregn-5-en-20-one) in which the expected ketones constituted only an insignificant proportion and the main bulk of the mixture consisted of the products of their further dehydrogenation and also the alcohol dehydrogenation products.

The formation of a mixture of products, noted for unsaturated alcohols, in a microreactor placed between the separating column and the mass spectrometer is undesirable, because the interpretation of the mass spectra of the unresolved mixture gives rise to difficulties. On the other hand, the method can be used effectively for saturated alcohols. For example, the dehydrogenation of 12α- and 12β-hydroxypregnanes (X), whose mass spectra are exceptionally non-characteristic, results in the formation of the same ketone (Xa), the intense peak with $m/z$ 233 in the mass-spectrum of which characterises the 12-oxo-group. As might have been expected, only two hydrogen atoms in this ketone are exchanged for deuterium:




The application of chromato-mass-spectrometry to the study of mixtures of diols and alkoxyalcohols is limited owing to their low volatility, poor chromatographic properties, and the relatively non-characteristic mass spectra. The RCMS methods described above are also unsuitable in this case. On the other hand, the conversion of such compounds into silyl ethers appears definitely promising. In order to increase the speed of the analysis, it is desirable to obtain the silyl ethers directly in the course of the chromato-mass-spectrometric analysis and not in separate experiments.

The method involving direct silylation in the chromatographic column and subsequent mass-spectrometric analysis has been used successfully in the study of a mixture of the aliphatic diols $HO(CH_2)_nOH$ ($n$ = 4–10) obtained synthetically.[42] *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% of added $(CH_3)_3SiCl$ was used as the silylating agent. It was added directly 5 s after the injection of the reaction mixture. The volume ratio of the specimen and BSTFA, amounting to approximately 1 : 3, ensured the quantitative silylation of the diols. The mass-spectrometric characteristics of the trimethylsilyl ethers of the diols were established, the molecular weights of the diols were determined, and the character of the alcoholic functions (whether they are primary or secondary) was deduced. Unfortunately, the mass spectra of the silyl ethers have no distinctive features which would make it possible to determine the structure of the carbon skeletons of the diols.

An analogous approach has been used in the study of mixtures of the alkoxyalcohols $RO(CH_2)_nOH$ (R = $CH_3$ or $t$-$C_4H_9$).[43] It was shown that the peaks of the $[M-CH_3]^+$ ions can be used to determine the molecular weights of the methoxyalkanols from the mass spectra of the trimethylsilyl

ethers. In the case of t-butoxyalkanols, the peaks of the ions $[M - C_4H_9]^+$ and $[M - C_4H_9O]^+$ can be used for these purposes.

The method of silylation directly in the chromatographic column can be used also for the investigation of other hydroxy-compounds (carbohydrates, steroid and terpene alcohols, lipid diols and triols, and acids).

## IV. INVESTIGATION OF DISSOCIATIVE IONISATION MECHANISMS

Deuterium-labelled analogues are used widely in the mass-spectrometric study of the mechanisms of the fragmentation of organic compounds. In all the known instances, preparative methods involving the isolation of the required products are used to obtain such derivatives. However, in certain cases the deuteriated analogues can be obtained directly in the injection system of the mass spectrometer without subsequent isolation. This procedure makes it possible to work with submicrogramme amounts of the test substance and sharply reduces the time of the investigation. Naturally, only those deuteriation methods are then permissible which ensure the selective introduction of the label into specific positions in the molecule. These requirements are satisfied by the above method in which reaction columns containing KOD are employed.

The mechanisms of the fragmentation of certain aliphatic ketones under electron impact have been investigated with the aid of a reaction column containing KOD dispersed in a stationary liquid phase and deposited on a solid carrier.[36] The starting materials were not the ketones themselves but the corresponding alcohols, which were subjected to preliminary dehydrogenation in a microreactor placed before the reaction column.

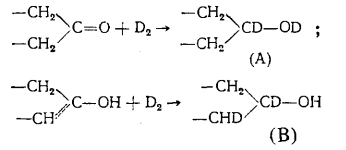
The reaction column, which contained $(Ph_3P)_3RhCl$ dispersed in Carbowax 20M on Chromaton and ensured the selective addition of deuterium to the double bonds of olefins under catalytic conditions, was used to investigate the mechanisms of the fragmentation of cyclobutane hydrocarbons.[44] The initial substrates employed were methylene-, vinyl-, and propylene-cyclobutanes. When these were passed through the above column in a stream of hydrogen or deuterium, the corresponding saturated hydrocarbons and their vicinal dideuterio-analogues were formed according to the mass-spectrometric data. Comparative analysis of the mass spectra permitted the conclusion that the $M^{\ddagger}$ species derived from the alkylcyclobutanes can decompose in both intact cyclic and acyclic forms. The decomposition of the former ensures the characteristic division of the ring "in half" with elimination of the $C_2H_4$ molecule. On the other hand, the elimination of any alkyl radical takes place after the isomerisation of $M^{\ddagger}$ to the open-chain acyclic form. The results obtained also indicate a low probability of the existence of the cyclobutyl cation in the gas phase.

The fragmentation of 1,1-dimethyl-1-silacyclopentane, 1-ethyl-1-methyl-1-silacyclobutane, and ethyltetraethoxysilane was investigated by an analogous procedure. Together with the corresponding dideuterio-analogues, these compounds had been obtained from 1,1-dimethyl-1-silacyclopent-3-ene, 1-methyl-1-vinyl-1-silacyclobutane, and triethoxyvinylsilane respectively.[45]

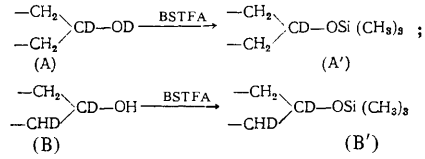
## V. INVESTIGATION OF HETEROGENEOUS CATALYTIC REACTIONS

The use of the microreaction technique and chromato-mass-spectrometry opens up wide prospects for the investigation of the pathways and mechanisms in heterogeneous catalytic reactions. In the course of a single experiment, it is possible to record by this method the chromatogram of the mixture of products (used for the quantitative estimation of the composition) and to obtain mass spectra permitting the high speed determination of the structures of the products. Although microreactors have been used for a long time in the study of catalytic reactions in combination with gas chromatography, this approach has not yet been as widely adopted in chromato-mass-spectrometry as it should despite its one significant advantage—it permits investigations using labelled compounds. The possibility of investigating by the RCMS method of reactions such as hydrogenation, dehydrogenation, hydrogenolysis, deoxygenation, etc., using deuterium is of undoubted interest. At present one can point to only one study where this method has been used to determine the mechanism of a heterogeneous-catalytic reaction and where its advantages have been fully manifested. It concerned the investigation of the mechanism of the hydrogenation of alicyclic ketones on a fused iron catalyst in a pulse microreactor → separating column → mass-spectrometer system.[46]

The hydrogenation of carbonyl compounds is known to proceed via the addition of hydrogen either to the carbonyl group (the ketone mechanism) or to the double bond of the corresponding enol (the enol mechanism). If the reaction takes place in a deuterium atmosphere, the isotopic forms of the alcohols (A) and (B) should arise respectively when these mechanisms operate:



In a direct mass-spectrometric study of the alcohols formed, it is not possible to establish reliably their isotope composition owing to the low intensity of the $M^{\ddagger}$ peaks, the presence of the peaks of the $[M-H]^+$ ions, and also the reverse D/H exchange of the active hydrogen atoms in the mass spectrometer. It has therefore been suggested[46] that the alcohols be silylated with the aid of BSTFA directly in the separating column. In this case the silyl ethers (A′) and (B′), with different numbers of D atoms which can be readily determined mass-spectrometrically, are then formed from the alcohols (A) and (B):



A special reactor containing an additional inlet for BSTFA was constructed for studies by the above procedure; in order to avoid the poisoning of the catalyst, the silylating agent was introduced into the gas stream beyond the catalyst layer but before the inlet into the chromatographic column.

Calculation of the isotope composition of the silyl ethers of the alcohols taking into account the isotope composition of the unreacted ketone established that the hydrogenation of cyclopentanone and cyclohexanone in the presence of the above catalyst in the temperature range 50–210 °C proceeds with equal probabilities via the enol and ketone mechanisms.

In carrying out such investigations, one must bear in mind that during chromatography different isotopic forms can be eluted in different ways (the forms enriched in deuterium are eluted more readily), although in the general

case the chromatographic zone is not resolved. In order to determine the true isotope composition, it is in this case necessary to scan repeatedly in the course of the elution of the test substance. The calculation is in this case based on the overall mass spectrum.

## VI. PYROLYTIC CHROMATO-MASS-SPECTROMETRY

The combination of pyrolytic methods with chromato-mass-spectrometry (PCMS) can be used for different purposes. In the first place PCMS is an effective procedure for the investigation of the mechanisms of the thermal decomposition of organic compounds.[47,48] From the standpoint of analytic possibilities, the application of the PCMS method to the study of the structures of high-molecular-weight compounds is of greatest interest. For the qualitative analysis of the composition of the pyrolytic reaction mixture, the PCMS method is much more effective than the pyrolytic mass-spectrometric method. However, it is not always suitable for the determination of the quantitative composition, because the volatility of the pyrolysis products may be low and they may not be eluted from the chromatographic column or their molecular weight may exceed the limit of the molecular weights detectable by the mass spectrometer. Nevertheless in some cases it is possible to establish by this method both the qualitative and the quantitative composition of the pyrolytic reaction mixture.[49]

The same pyrolysers (pyrolysers based on the Curie point and filamental and tubular pyrolysers) are used in PCMS as in pyrolytic mass-spectrometry or pyrolytic gas chromatography.[3,4]

In terms of the speed of analysis, PCMS is inferior to pyrolytic mass spectrometry, but the level of structural information obtained in the former case is undoubtedly much greater. The determination of the structures of the pyrolysis products and on that basis also of the structures of high-molecular-weight compounds can be evidently facilitated by using the additional chemical methods discussed above.

The efficiency of the method has been demonstrated in relation to the study of polychloroprene, polyisoprene, a polynitrile, and other industrial elastomers.[50] In the study of the copolymers of acrylonitrile and styrene by this method using a capillary column, the monomers, dimers, and trimers were identified mass-spectrometrically.[51] Analysis of the data obtained made it possible to infer the sequence of units in such polymers.

Very important information, of both theoretical and practical value, has been obtained in the study of coal by the PCMS method.[52] Various saturated and unsaturated hydrocarbons, aromatic hydrocarbons, and phenols were identified among the pyrolysis products.

Although the pyrolytic mass-spectrometric method is used widely in the study of biopolymers, there have been virtually no studies using the PCMS method for this purpose. This is most likely to be due to the high polarity of the pyrolysis products formed, which are poorly eluted in gas-chromatographic separation. Presumably the use of intracolumn derivatisation will render such objects susceptible to analysis also by the PCMS method. In addition, the PCMS method using liquid chromatography may prove to be promising for the investigation of biopolymers.

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# Outer-sphere Complexes in Analytical Chemistry

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Published data on the use of outer-sphere complexes, formed from coordinatively saturated inner-sphere complexes and ligands, cationic species, or molecules of organic solvents present in the outer sphere, in present-day analytical chemistry have been reviewed. The characteristic features of the outer-sphere complexes, namely their relatively low stability and low activation energy for reactions in the outer sphere, together with their variety, make these complexes effective for the separation, isolation, and more particularly determination of inorganic and organic substances. The consequent improvement in the sensitivity, selectivity, and speed of analytical determinations has been discussed.
The bibliography contains 277 references.

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## INTRODUCTION

In recent years there has been a considerable increase in interest in the practical application of outer-sphere complexes (OC) and the concepts of outer-sphere coordination in analytical chemistry. This is related to the need to solve a large number of urgent practical problems, which requires considerable improvement of traditional methods and techniques of analysis, based on non-trivial approaches and new theoretical concepts. Significant improvement of the sensitivity and selectivity, lowering of the detection limits, and decrease in the time taken for analysis can be achieved using the chemical-analytical properties of OC. There are practically no published reviews of the use of OC in analytical chemistry, however. The information in the published review[1] and monographs[2,3] deals mainly with the use of OC only in the photometric analysis of inorganic substances, whereas the role of OC in present-day analytical chemistry is much more significant and varied.[4] Progress in the chemistry of OC[5-11] makes it impossible to re-examine published data on the interesting analytical possibilities provided by this group of compounds.

Outer-sphere complex formation is used to obtain analytical information on the object of analysis not only in photometry[3,12-14] and fluorimetry,[3,13-17] but also in extraction methods,[13,18-20] ionometry,[21-24] and chromatography.[25-28] OC are also used in the trace analysis of elements,[29] in methods for concentrating micro-elements,[30-32] in the chemistry of organic reagents,[3] and in the analysis of various organic substances.[33-35] They are used as analytical forms in crystal-microscopy,[36] qualitative and gravimetric analysis,[37,38] titrimetry,[39,40] work in aqueous-organic solutions,[39-44] automatic analysis,[45-47] and in other situations.[48,49] The analytical use of OC therefore constitutes a fairly

extensive and independent field of application of complex compounds in analytical chemistry. The unique nature of the chemical-analytical properties of OC is determined by the characteristic features of coordination in the outer sphere and by the thermodynamic properties of these compounds. It is therefore appropriate to examine briefly those aspects of the chemistry of OC of greatest importance for analytical purposes.

## II. THE CHARACTERISTIC FEATURES OF OUTER-SPHERE COMPLEXES—THE BASIS OF THEIR ANALYTICAL APPLICATIONS

Published definitions of OC are not unambiguous. Usually, OC are defined as compounds formed by the attachment of electrically neutral[2] or charged[3] ligands to a coordinatively saturated complex. The features emphasised range from the absence of a bond between the outer-sphere ligand and the central atom[5,10,50–53] to the identification of OC with ion pairs.[54–56] The ambiguity of the definition was eliminated in a paper[57] which reflects the many years' experience of the Leningrad school in the study of outer-sphere complex formation. The fundamentally important fact is that an OC is formed by an inner-sphere complex, saturated with respect to its coordination number, and *any* species in the outer sphere. A new direct chemical bond with the central atom of the original reagent is not formed, since the reaction in the outer sphere and the direct chemical bonding take place between the ligands of the inner sphere and the species in the outer sphere. The species of the outer sphere can be described in general terms as ligands—electron pair donors or acceptors[59]—possibly reflecting present-day concepts of the coordinate bond.[60] A characteristic feature of OC is their definite stability towards solvolytic dissociation in polar solvents, characteristic of complex compounds in general.[61]

Ion pairs differ from OC;[53,57–59] ion pairs are produced as a result of the Coulombic interaction of partly or completely solvated ions, whereas OC are formed by a donor–acceptor interaction and show appreciable signs of covalent bonding.[58] The change in the potential energy of the system with change in the distance between the ions in ion pairs is smooth. In the ionisation of OC, however, it is necessary to overcome a potential barrier, whose magnitude is determined by the activation energy,[62] which is low for reactions in the outer sphere.[8,56,57] Thus it is possible in principle for ion pairs and OC to coexist in solution.[53]

The coordinating centre of OC of interest for analytical chemistry are usually inner-sphere cationic or anionic complexes[7,8,10] or neutral chelates.[26,27] The variety of outer-sphere species, which may be anionic complexes[63] or the neutral molecules of organic reagents or solvents,[11] which have electron-donor properties, or the cations of organic bases,[57] which have electron-acceptor properties, is apparently responsible to a large extent for the fairly extensive occurrence of OC. The characteristic features of these compounds used in analysis cannot be attributed entirely to electrostatic interaction. OC also differ from anisotropic[2,10] and mixed-ligand[3] complexes, although this is not always taken into account in the examination of their analytical applications.[1] The anionic complexes of metals, forming the coordination centres of the corresponding OC, do not always contain the number of acido-ligands specified by the coordination number of the metal ion.[5,57] Outer-sphere complexes containing complex forms of the same metal in the inner and outer coordination spheres have been called polycomplexes.[64] The inclusion of OC among the so-called "super-complexes"[65] has been regarded as inappropriate.[10]

The problem of the nature of the chemical bond in the outer sphere is complex. Donor–acceptance interaction makes the most important contribution, and the electrostatic contribution constitutes only part of the outer-sphere forces.[8,11,53,56–59,66] In general, it is recommended that account be taken of ion–dipole interaction, hydrogen bonding, covalent bonding, forces of structure formation in the solvent, dispersion forces, and the influence of external electric fields.[56] Problems of outer-sphere coordination and its experimentally detectable effects in solutions and crystals have been examined.[8–11,14,56–59,66,67]

The three-dimensional delocalisation of one-electron states, a characteristic of the coordinate bond,[60] is revealed by the fact that the points of contact between the outer-sphere ligands and the inner-sphere complexes are usually the points with the highest effective charges of the interacting species.[10] The appearance of or a change in a charge-transfer band in the electronic spectra of OC are regarded as fairly clear signs of outer-sphere coordination.[8,10,57,58] Charge transfer is due to the mixing of the wavefunctions of closely situated excited and ground states, so that in the systems being considered it corresponds to a greater or lesser covalent contribution to the chemical bonding in the outer sphere. This phenomenon has been described, for example, for a large number of OC based on metal–phenanthroline complexes[3] and the OC of hexammineruthenium(III) with various substituted pentacyanoferrates.[68]

The stereoselectivity of outer-sphere complex formation by Λ-(+)- and Δ-(−)-tris(ethylenediamine)cobalt(III) with the Δ-(glycinato)bis(oxalato) cobaltate(III) anion,[69] the localised attachment of fluoride and chloride ions in the outer sphere of hexasolvates of aluminium in methanol and ethanol,[70] and the outer-sphere coordination of pyridine molecules to the hexasolvate of cobalt(II) in deuteriated methanol, established by spin–lattice relaxation,[71] can also be related to the appearance of covalent interaction in the outer sphere. The specific nature of the outer-sphere forces, associated with charge transfer to antibonding orbitals of the inner-sphere complex and with dispersion interaction, is also confirmed by the explanation for the increase in the stability of the OC of tris(2,2′-bipyridyl)cobalt(II) with ammonia, methylamine, and ethylamine with increase in the complexity of the ligand.[72] The three-dimensional oriented solvation of the molecules of coordinatively saturated transition metal chelates by organic solvents determines the energetically most favourable position of the ligands in the outer sphere of these OC.[11] The calculated effects of the redistribution of electron density in hexakis(dimethylformamide)iron(III) and hexakis(dimethylthioformamide)iron(III) perchlorates differ considerably.[73]

Among OC with an electron-acceptor species in the outer sphere, the compounds of greatest interest for analytical chemistry are those formed by metal acido-complexes with the outer-sphere cations of onium compounds and basic organic dyes, referred to in the literature as ionic associates. Recent papers[67,74–76] indicate that electrostatic theories cannot explain the properties of these compounds. The covalent contribution to the bonding in the outer sphere in these systems is indicated, in particular, by the interpretation of the charge-transfer bands in their electronic spectra.[67] Data of this kind have been published, for example, for the compounds formed by anionic halogeno-complexes of copper(II), iron(II), cobalt(II), mercury(II), palladium(II), and silver with the doubly-charged cation of N,N′-dimethyl-4,4′-bipyridyl,[74] for the OC of hexacyanoferrate(II) ions with the cations of various heterocyclic

amines,[75] for the OC of pentacyanoferrate with coordinated dimethyl sulphoxide and pyridine molecules[76] and for other similar complexes.[77] The outer-sphere coordination of electron-pair acceptors by hexacyanoferrate(II,III) ions is indicated by the displacement of the half-wave potential to more positive values.[53] The specific nature of the inter-ionic interaction of 2-octylpyridine with various anions is revealed by the decrease in the polarisation of the π-electron cloud of the aromatic cation and the formation of hydrogen bonds with them, in particular with the tetrachlorogallate ion.[67]

There is practically no corresponding published information on compounds with the acceptor species of a basic dye in the outer sphere. It has been suggested that there are localised contacts between the cations of these dyes and anions as a result of the irregularity of the electron density distribution in the former and the increase in the contribution of ion–dipole interaction to the chemical bonding.[3] Other factors possibly of importance are the type of hybridisation of the atomic orbitals in the acido-complex, which determines its geometry; the difference in the electronegativities of the central metal atom and the donor atom of the inner-sphere ligand, which determines the distribution of the atomic charges in these anions;[78] and the increase in the stability of the OC as a result of the forces of structure formation in the solvent.[79] This is consistent with data on the stability of compounds of $BF_4^-$ (calculated charge on the fluorine atom −0.63[78]) with the cations of basic dyes. The stability constants (lg β) of OC increase in the order Methyl Green, Fuchsine, Malachite Green, Brilliant Green, Crystal Violet: 1.8, 2.0, 2.0, 2.6, and 3.2 respectively.[80] The OC with the most symmetrical species in the outer sphere has the highest stability. The stability of the OC of $SbCl_6^-$ with the cation of Crystal Violet is noteworthy; this complex is decomposed completely only in concentrated ammonia.[13]

The stability constants of the outer-sphere compounds of cationic complexes of metal ions with various ligands have been systematised.[10] Most of the data relate to compounds based on inert inner-sphere complexes of $Co^{III}$ and $Cr^{III}$. There is much less published information on the OC of iron(II,III), nickel(II), and the platinum metals,[10] and for OC formed by neutral chelates with the molecules of organic solvents in the outer sphere.[11] The literature on analytical chemistry contains no examples of the practical application of the tabulated stability constants of OC.

The concentration stability constants of various OC formed by the aquo-ions of the alkali and alkaline earth metals with polyatomic anions in aqueous-organic solutions[81] are provisional, since they were calculated without allowance for side reactions. In these systems, because of the lability of the coordination centre, it is particularly important to distinguish the effects of outer-sphere and inner-sphere complex formation; this is an extremely complex problem, which has not been fully resolved.[8]

The specific nature of the properties of OC as chemical compounds determines their practical importance in analytical chemistry.

## III. THE CHEMICAL-ANALYTICAL PROPERTIES OF OUTER-SPHERE COMPLEXES

In analytical chemistry, outer-sphere complex formation reactions and OC themselves are used in various methods for the qualitative detection, quantitative determination, isolation, and separation of inorganic ions and organic substances.

### 1. Principal Fields of Application of Outer-Sphere Complexes

The analytical application of OC depends on processes in solution in which these complexes are reaction products or, less frequently, the starting materials. The use of OC in analysis is determined by their characteristic properties, which enable these compounds to be the material carriers of analytical signals. These characteristic properties are low solubility in water and higher solubility in organic solvents; characteristic crystal shape; the ability of OC, containing the element being determined, to be coprecipitated; intense absorption in the visible or ultraviolet ranges of the spectrum or bright fluorescence; and the ability of OC to undergo flotation at the interface between two immiscible solvents or extraction into an organic phase. Another form of application of OC involves the production of an indirect analytical signal by a change in the concentration of the ions forming the OC, or its fulfilment of a "transmitting" function with respect to this signal by the selective ionisation of the OC in the outer sphere, often in conjunction with a dynamic process. This becomes possible because of the low thermodynamic stability of OC and the low activation energy of ligand replacement processes in the outer sphere. OC and the reactions involved in their formation are therefore used to produce indirect analytical signals in titrimetric methods with different techniques for establishing the end point—photometric,[39–44,82] amperometric,[83,84] conductometric,[85] potentiometric,[82] and others.[86,87] These characteristic features of OC play an important role in their use as electrode-active materials in the membranes of liquid ion-selective electrodes, in extensively repeated sorption and desorption processes in chromatographic separation systems, and in the rapid formation of OC in flow-type automatic analysers.

An intense analytical signal resulting from the formation of OC, for example their strong absorption or bright fluorescence, makes it possible to achieve a fairly low detection limit.[12–17] The marked dependence of the properties of OC on the nature of the metal ion and the inner- and outer-sphere species often makes it possible to achieve a high selectivity in the determination. Examples can be found in various fields of application of OC—ionometry,[21–24] ligand-exchange[25,88] and other forms of liquid chromatography,[26–28,69,89,90] and titrimetry in aqueous-organic solutions.[39–44]

OC with inert and labile inner coordination spheres have different chemical-analytical properties, and this must be taken into account in analytical practice. The situation is simpler in the first case, since in the analytical determination the OC dissociates only in the outer sphere. In the second case, dissociation of the OC in the inner sphere is also possible, and to suppress this and to ensure the maximum yield of the analytical form, an excess of the inner-sphere ligand is added to the solution.

Dilute aqueous solutions of most salts of *s*-, *p*-, and *d*-block elements, in which the anions are most frequently singly charged, contain only OC at concentrations below the limit of complete solvation.[8] Many reactions, therefore, for example complex formation[2,8,57,91] and redox reactions,[92,93] pass through a stage involving the decomposition of the OC of the aquo-ions of the metals and (or) the formation of intermediate OC. The formation of these OC as sources of analytical signals has no practical value, so that the kinetic role of OC is not examined in the present review.

The analysis of published data on the analytical applications of OC makes possible their systematisation, apparently for the first time. The results are given in Table 1, which shows the great variety of types of OC finding practical applications, although their use is not equally important in different analytical methods. Specific examples are examined below.

### 2. The Precipitation of Sparingly Soluble Outer-Sphere Complexes

The inner-sphere complexes of metals have low hydration energies, so that they can react with fairly large outer-sphere counter-ions to form neutral OC which are relatively sparingly soluble in water. This characteristic feature of OC was apparently first used by Bjerrum to separate thiocyanate complexes of chromium(III) by precipitating with quinolinium sulphate.[94]

Table 1. Fields of application of outer-sphere complexes in analytical chemistry.[1-4,12-28,30-35]

| Outer-sphere complex | | outer-sphere species |
|---|---|---|
| Fields of application | coordinating centre | |
| $ML_n^{x+}$, $ML_{n-k}L_k^{*x+}$ | $A^{y-}$, $R^{y-}$ | ph, e.ph, fl, e.fl, p, g, e, c, i.ch |
| » | $M^*X_m^{y-}$, $M^*X_{m-k}A_k^{y-}$ | ph, e.ph, p, g, lig.ch |
| $MQ_q^{x+}$ | $A^{y-}$, $R^{y-}$, $M^*X_m^{y-}$, $M^*R_n^{y-}$ | ph, e.ph, fl, e.fl, c, i, flot, p, g, i.ch |
| $MQ_q$ | *m*Solv, HO—Si≡ | e, liq.ch |
| $M(OH_g)_n^{x+}$ | $A^{y-}$, $M^*X_m^{y-}$, $\mathscr{M}-A^{y-}$ | aq-org, i.ch |
| $M^{x+}\cdot$Solv | $A^{y-}$, $M^*X_m^{y-}$ | e, aq-org |
| $MX_m^{y-}$, $MX_{m-k}X_k^{*y-}$ | $D^{x+}$ | e.ph, e.fl, flot. c, i |
| » | $B^{x+}$, $Z^{x+}$ | e, flot, c, i |
| » | $\mathscr{M}-B^{x+}$ | i.ch, lig.ch |

Notation: M = metal, L and Q = unidentate and multidentate ligands, A = outer-sphere ligand, R = anion of coloured reagent, X = acido-ligand, $D^{x+}$, $B^{x+}$, $Z^{x+}$ = cations of a basic dye, an organic base, and an onium compound respectively, ≡ = ion-exchanger matrix, HO—Si = silica gel, Solv = organic solvent; ph = photometry, e.ph and e.fl = extraction photometry and extraction fluorimetry, fl = fluorimetry, p = precipitation, g = gravimetry, e = extraction, c = coprecipitation, flot = flotation, i = ionometry, aq-org = reactions in aqueous organic solvents, lig.ch, i.ch, and liq.ch = ligand-exchange, ion-exchange, and liquid chromatography.

Quantitative data on the solubility of sparingly soluble OC, usually in the range $10^{-3}$–$10^{-5}$ M, are rarely used as a basis for their analytical application. They are most frequently determined by studying the OC equilibrium by the solubility method,[95,96] or the thermodynamics of transfer.[97,98] The least soluble OC are important in analysis. The solubility of OC in water is lower, the larger their component fragments. For example, at 25° the solubility of hexamminecobalt(III) oxalate is $3.9 \times 10^{-4}$ M,[99] and that of octammine-μ-aminohydroxodicobalt(III) chloride sulphate is $10^{-7}$ M.[100] The solubility of OC can be calculated from the solubility product;[95,96,101,102] more accurate determination requires allowance for the stability of the OC in solution and the contribution of side reactions of the coordinating centre and the outer-sphere ligands.[102] With increase in the ionic strength of the solution, the solubility of OC increases slightly.[95,96,102] The compounds of metal acido-complexes with outer-sphere organic cations, containing larger species, are less soluble. For example, the solubility of the OC of $CdI_4^{2-}$ with Chromopyrazole is $0.87 \times 10^{-3}$ M, and that with Chromopyrazole II is $7.2 \times 10^{-6}$ M.[103] The more hydrophobic the inner- and (or) outer-sphere species, the greater the solubility of the OC in an aqueous-organic solvent.[98]

The precipitation of OC is widely used in the identification of ions[37,38] and pharmaceutical products,[33] crystal-microscopy,[36] gravimetric analysis, and different forms of precipitation titration, and to separate elements. A particular field of application is the concentration of micro-elements by coprecipitation and flotation.

The element being determined is most frequently present in OC in the inner-sphere complex, and less frequently as the outer-sphere species. Data on OC used as gravimetric forms are given in various sources, including a series of monographs.[49,82,84,86,104-124] The directed selection of the ligands or species of the outer and inner coordination spheres makes it possible to achieve the required analytical effect relatively easily. Thus hexamminecobalt(III) is used for the gravimetric determination of anionic forms of beryllium,[107] cobalt,[82] chromium(III),[110] indium,[111] phosphorus,[115] rhodium(III),[86] and uranium,[122] and the outer-sphere coordination of organic bases by the anionic complexes of elements makes it possible to determine silver,[104] gold,[105] cadmium,[109] mercury,[84] zinc,[124] and other metals.[86,117,121,123] The use of OC in gravimetric analysis extends the possibilities provided by the method and makes it possible to obtain gravimetric forms with a high molecular mass, decreasing the conversion factor and increasing the accuracy of the analysis, particularly in the determination of small quantities of elements. For example, it is possible to determine down to 5 mg of silver or molybdenum as $[Co(en)_2 \cdot (SCN)_2][Ag(SCN)_2]$ (en = ethylenediamine) and $[Cr(NH_3)_5 \cdot Cl](MoS_4)$ respectively[104,114] or down to 2 mg of palladium as $[Pd(SCN)_4][(C_4H_9)_4N]_2$.[116] In qualitative reactions the detection limit is fairly low, amounting to fractions of a microgram.[36-38]

The precipitation of OC is in general not very selective. It is possible to achieve selective precipitation by using different combinations of ligands in complex inner- and outer-sphere species. For example, nickel, copper, iron(III), zinc, and cobalt do not interfere in the determination of gold as bis(trimethyl)hexamethylenediammonium bromoaurate.[105] The gravimetric determination of uranium as $[Co(NH_3)_6]_2[UO_2(CO_3)_2](H_2O)_3(NO_3)_2$ is highly selective.[122] Selective precipitation is used to isolate and separate various elements; for example the precipitation of sulphates by octammine-μ-aminohydroxodicobalt(III) chloride for their indirect photometric determination,[100] the separation of tellurium from selenium as $[Te(phen)_3]X_4$ (phen = 1,10-phenanthroline, X = $Cl^-$, $Br^-$),[125] tantalum from niobium as $[Fe(phen)_3](TaF_7)$,[126] and niobium from tantalum by precipitating $[Fe(phen)_3][NbO_2(C_4H_5O_5)_2]$ from tartrate solution.[127]

Precipitation titration methods based on the formation of sparingly soluble OC, with different means of establishing the end point, are widely used, for example to determine cobalt,[82] silver,[85,104] platinum,[86] anionic complexes of cadmium,[109] tin,[119] mercury,[84] boron, iron(III), gold, and other elements using quaternary ammonium bases[87] and onium salts.[128] High sensitivity in the determination is achieved in the amperometric titration of $BiI_4^-$ with the protonated 8-quinolinol cation[83] and of zinc with thiocyanate ions in the presence of diantipyrinylmethane and its analogues, and even in the visual titration of $Zn(SCN)_4^{2-}$ with Chromopyrazole.[124]

Indirect titrimetric methods based on the preliminary precipitation of OC[108,109,112] have now lost their importance. It is possible, however, to determine down to 15 μg bismuth by precipitating as $[Bi(SCN)_6][(C_4H_9)_4N]_3$ after treating

the precipitate with hydrogen carbonate and titrating thiocyanate ions in an amplification reaction which gives 114 moles of iodine per mole of metal.[129]

OC are effective for concentrating elements. The marked structural similarity between various sparingly soluble OC and the corresponding organic collectors[31] ensures a high degree of coprecipitation of elements in the outer or inner coordination spheres. For example, 90% plutonium(IV) is coprecipitated as the OC of $Pu(NO_3)_6^{2-}$ with the Butylrhodamine cation using Butylrhodamine nitrate as collector; the detection limit is 0.02 μg Pu in 200 ml of solution. The same degree of separation is achieved for silver as the OC formed by its dithizone chelate with azo-dye anions in the outer sphere, and also for other elements as various OC.[31] In the coprecipitation of cobalt, molybdenum, zinc, and lanthanides with salts of antipyrine dyes in the presence of thiocyanate ions, competition between the ligands for a place in the inner sphere, and the formation of two types of coprecipitated OC, are possible.[130,131] The OC of metal–phenanthroline complexes with singly-charged anions in the outer sphere are effectively coprecipitated with AgX (X = $Cl^-$, $Br^-$, $I^-$, $SCN^-$), making it possible to achieve an absolute concentration enrichment coefficient of $10^3$.[132]

Various OC with hydrophobic species in the inner or outer spheres have amphiphilic properties, so that they can be concentrated by flotation, usually with photometric analysis in the final stage. The flotation of OC based on metal–phenanthroline complexes has been examined in a monograph.[3] By carrying out this process at the interface between water and a mixture of toluene and carbon tetrachloride, using the bismuth–Alizarin Red–Brilliant Green system, it is possible to determine down to $10^{-4}$% bismuth in arsenic salts with a detection limit of 0.5 μg Bi in 25 ml of solution.[133]

Examples of the use of sparingly soluble OC in analytical chemistry are given in Table 2.[49,86,110,112,130–136]

### 3. Outer-Sphere Complexes in Photometry and Fluorimetry

The OC used in photometric and chemical luminescent analysis are extremely varied, because of the ready production, on the basis of these compounds, of analytical forms (see Table 1) showing strong absorption in the visible and ultraviolet ranges of the spectrum, or bright fluorescence. The absorbing centre in these OC may be the inner-sphere complexes (the coordination unit of the OC), the outer-sphere species, or both partners of the photometric reaction. Fluorescence is most frequently produced in outer-sphere cations. The element being determined is usually in the inner-sphere complex, and is less frequently a component of the outer-sphere species. Coloured and fluorescent OC are usually extracted by organic solvents, and this makes it possible to carry out multiple extraction-photometric and extraction-fluorimetric determinations.[1–3,12–17,33,34,137–142] The compounds formed are usually ionic associates. The inadequacy of traditional views of these compounds has been noted in an examination of the properties of the OC of metal–phenanthroline complexes with various outer-sphere ligands.[2,3] In recent years there has been a greater tendency to regard the production of the analytical forms being considered here as the result of the interaction of complex electronic systems, and not individual oppositely charged ions.

In photometry and fluorimetry, extensive use is made of OC with the molecules of heterocyclic polyamines in the inner sphere; the wide range of outer-sphere ligands in these complexes makes it possible to develop an extremely large number of methods for determining various elements.[3,14] The nature of the outer-sphere ligands in these OC is important, since it determines the ability of the analytical form to undergo extraction, and the selectivity of the determination. The high extractability of $[Fe(phen)_3]X_2$ (X = $BF_4^-$, $ClO_4^-$), which in the case of the perchlorate ion correlates with the stability of the OC,[143] has been used to determine these anions.[49,85] The detection limit for various elements, achieved using OC, is fairly low, for example 0.07 μg Co in 6 ml of solution in the determination of cobalt as the OC of its phenanthroline complex with hydroxyxanthene dyes[144] or $10^{-5}$ μg Ru in 1 ml of solution in the determination of ruthenium(II) as $[Ru(phen)_2]Cl_2$ by a luminescent method.[145] In the last case the covalent hydration of the inner-sphere ligand, leading to the formation of the carbinolamine, increases the fluorescence of this OC. The possibility of cooperation (that is outer-sphere coordination of ligands in the OC of metal–phenanthroline complexes with dye anions, which excludes the mutual displacement of ligands, has been examined.[146] The inner coordination sphere of a coloured OC may be more complex, as observed, for example, in the extraction-photometric determination of iron(III), bismuth, indium, gallium, and various other elements as $[M(PAR)(ANT)_3]ClO_4.nCHCl_3$ (PAR = pyridylazoresorcinol, ANT = antipyrine). The dependence of the extractability of these OC, the optical characteristics of the extract, and the solvation number on the nature of the anion of the outer sphere has been determined.[142] The outer-sphere complexes $[ReO(thur)_3Cl_2]Cl$ and $[ReO(thur)_4.Cl]Cl_2$ (thur = thiourea) have been used as analytical forms in the determination of rhenium;[117] the compound $[BiSO_4.(oxin)_3]X_4$ (oxin = 8-quinolinol; X = $Cl^-$, $Br^-$, $I^-$, $ClO_4^-$, etc.) in the precipitation-photometric determination of bismuth;[147] and $[Co(NH_3)_2(NO_2)_4][(C_6H_{13})_4N]$ in the indirect determination of perchlorates by exchange extraction (from the decrease in the intensity of the colour of the organic phase).[85]

In extraction photometry and fluorimetry, extensive use has been made of associates of anionic complexes of elements with outer-sphere coloured or fluorescent cations of aryl-, diaryl-, and triarylmethane, xanthene, acridine, arylamine, antipyrine, azo, cyanine, and other dyes.[12–17,137–142] The selectivity of the determination depends on the nature of the outer-sphere anionic complex of the element, and its sensitivity on the intensity of the colour of the outer-sphere species. For example, gallium in zinc was determined by converting the element being estimated into an anionic complex with pyrocatechol, followed by extraction as the OC with basic dyes.[148] The detection limits achieved in these methods are extremely low,[8,12–17] for example 0.03 μg $ml^{-1}$ for uranium(VI),[149] 0.02 μg $ml^{-1}$ for scandium,[150] 24 μg $ml^{-1}$ for magnesium,[151] and $10^{-4}$ μg $ml^{-1}$ for gallium (extraction-fluorimetric method).[160,161] Examples of the use of other OC which make it possible to improve considerably the analytical characteristics of reactions[149–167] are given in Table 2.

A correlation is observed between the stability constants of OC and the molecular refraction of the inner-sphere ligands, which is a function of their average polarisability. This confirms the possibility of the outer-sphere coordination of the cations of Rhodamine S by anionic complexes of the lanthanides with substituted salicylic acid and 8-quinolinol,[152] and also other basic dyes in similar systems.[148–153] The displacement of the absorption band in the spectra of these OC is attributed to the difference in their stabilities in the ground and excited states.[15] The hypsochromic shift of 10–20 nm in the spectra of the outer-sphere cations of antipyrine dyes in compounds with $AuCl_4^-$ [158] and of

**Table 2.** Principal fields of application of outer-sphere complexes in analytical chemistry.

| Species being determined | Coordinating centre of the OC | Outer-sphere species | Method of determination* | Refs |
|---|---|---|---|---|
| P | $[Co(en)_3]^{3+}$ | $HP_2O_7^{3-}$ | g | [49] |
| Pt | $[Pt(thur)_4]^{2+}$ | $[Cr(SCN)_4(NH_3)_2]^{2-}$ | g | [86] |
| Cr | $[(NH_3)_5CoO_2 \cdot Co(NH_3)_5]^{5+}$ | $Cr_2O_5^{2-}$ | g | [110] |
| Ge | $[Cd(phen)_3]^{2+}$ | $[Ge(C_6H_4O_2)_3]^{2-}$ | g | [112] |
| Co, Mo, Zn, Ln | $[M(SCN)_n]^{x-}$ | antipyrine dye | c, emis | [130] |
| Nd, Sm, La | $[Ln(diantipyrinylmethane)_3]^{3+}$ | $SCN^-$ | | [131] |
| Tl | $TlBr_4^-$ | acridine | flot, ph | [134] |
| Tl | $TlCl_4^-$ | papaverine | | [135] |
| Pt, Pd, Au | $MCl_n^-$ | cetylpyridinium | flot | [136] |
| Hg | $[Hg(phen)_3]^{2+}$ | Bromophenol Blue | e.ph | [146] |
| U | $[UO_2(oxin)_3]^-$ | Butylrhodamine | e.ph | [149] |
| Sc | $[Sc((NO_2)_2oxin)_3]$ | Rhodamine S | e.fl | [150] |
| B | $[B(mandelic\ acid)_n]^-$ | Malachite Green | e.ph | [153] |
| Pt | $PtCl_4^{2-}$ | Methyl Green | » | [154] |
| Au | $AuBr_4^-$ | Chromopyrazole I | » | [157] |
| Au | $AuCl_4^-$ | Antipyrine dye | » | [158] |
| Ga | $GaCl_4^-$ | Rhodamine, Acridine Orange | e.fl | [160, 161] |
| Au | $AuCl_4^-$ | Acridine Yellow | e.ph | [162] |
| Sb | $SbCl_6^-$ | Acridine Orange | » | [163] |
| Bi | $BiI_4^-$ | azomethine dye | » | [164] |
| Co | $Co(SCN)_4^{2-}$ | Brilliant Green | ph | [166] |
| Bi | $BiO(S_2)_2^-$ | cetyltrimethylammonium | e.ph | [167] |
| Ru | $[Ru(phen)_3]^{2+}$ | $SCN^-$ | » | [176] |
| Cu | $[Cu(biquinolyl)_2]^+$ | $ClO_4^-$, nitroso-R-salt | » | [177] |
| Cu | $[Cu(phen)_3]^+$ | dibromofluorescein | » | [174] |
| Fe | $[Fe(phen)_3]^{2+}$ | pelargonic acid | » | [175] |
| Cu | $[Cu(SCN)_4]^{2-}$ | $[(C_4H_9)_4N]^+$ | e.ph | [179] |
| Ag | $[Ag(Cadion\ 2B)]^-$ | Triton X-100 | » | [181] |
| Hg | $[Hg_3(Xylenol\ Orange)_2]^{2-}$ | Amberlite A-2 | » | [182] |
| Ce | $CeX_n^{3-}$ (X=Cl⁻, $NO_3^-$, $SO_4^{2-}$) | cetyltrimethylammonium | e.ph | [189] |
| Tl | $TlCl_4^-$ | Brilliant Green | e, at.abs | [197] |
| In, Tl ... | $MCl_4^-$ | Aliquat | e | [200] |
| Be | $[(OH)_2Be(malonate)_n]^{2-}$ | » | e.ph | [201] |
| Os, Ru | $M(SCN)_6^{3-}$ | mesityl oxide | e, ph | [202] |
| $ClO_4^-$, $NO_3^-$ | $[Cu((CH_3)_2phen)_3]^+$ | $ClO_4^-$, $NO_3^-$ | e, at.abs | [49] |
| Cu | » | $SO_4^{2-}$, picrate | i | [207] |
| Au, Ag | $[M(thur)_2]^+$ | $[Co(NO_2)_4(NH_3)_2]^-$ | » | [208] |
| » | $M(CN)_4^-$, $MCl_2^-$ | Rhodamine B | » | [209] |
| Ag | $Ag(CN)_2^-$ | tetradecylphosphonium | » | [210, 211] |
| Au | $AuCl_2^-$, $Au(CN)_4^-$ | tetraphenylarsonium | » | [212] |
| Zn, $SCN^-$ | $Zn(SCN)_4^{2-}$ | tributyloctadecylammonium | » | [213] |
| Ag | $Ag(CN)_2^-$ | hexadecyltrioctylammonium | » | [214] |
| Ga | $GaCl_4^-$ | Ethyl Violet | » | [215] |
| Ta | $TaF_6^-$ | cetylpyridinium | » | [216] |
| racemates of Co(III) complexes | Λ-(+)-,Δ-(−)-$[Co(en)_3]^{3+}$ | Δ-(glycinato)-bis(oxalato)-cobalt(III) | lig.ch | [69] |
| racemates of organic acids | Λ-(+)-,$[Co(en)_2(NO_2)_2]^+$ | Λ-(+)-, Δ-(−)-anions | » | [224] |
| racemates of complexes | » | Λ-(+), Δ-(−)-$[M(C_2O_4)_3]^{3-}$ | » | [224] |
| dinucleotides, cephalosporins | ≡SiA—R—[en $Co(en)_2]^{3+}$<br>≡SiO—R—[en $Co(phen)_2]^{3+}$ | anions of dinucleotides and cephalosporins | » | [225] |
| Au | $AuBr_4^-$, $Au(SCN)_4^-$ | ≡Si—O—Si$(CH_2)_3$ $(NHCH_2CH_2)NH_2$ | liq.ch | [159] |
| acetylacetonates, etc. | chelate of Co(III), Cr(III) | di-isopropyl ether, HO–Si≡ | » | [26, 27] |
| metal chelates | » | chloroform, HO–Si≡ | » | [228] |
| Al, In, Ga... | $[M(Xylenol\ Orange)_n]^-$ | anion-exchanger groups | i.ch | [232] |
| alkaloids | $[Cr(SCN)_4(NH_3)_2]^-$ | alkaloids | e, at.abs | [35] |
| aminoacids | $[Ni(phen)_3]^{2+}$ | aminoacids | e, at.abs | [35] |
| benzylpenicillin | $[Cd(phen)_3]^{2+}$ | benzylpenicillin | » | [35] |
| polyhydroxyethylene surfactants | $[Fe(SCN)_6]^{3-}$ | surfactants | e.ph | [185] |
| V, Ta, Nb, Sb, P | $[K((CH_3)_2SO)_n]^+$ | $VO_2F_3^{2-}$, $TaF_7^{2-}$, $NbOF_6^{2-}$, $SbF_6^-$, $PF_6^-$ | aq-org, ph.titr | [41] |
| Al, In, Ga, Tl, B | » | $MF_4^-$ | » | [266] |
| Ti | » | $TiF_6^{2-}$ | aq-org, ph.titr | [271] |
| Pd, Pt | » | $PdCl_4^{2-}$, $PtCl_6^{2-}$ | » | [43] |
| benzenesulphonates | $[Ba(OH)_2)_6]^{2+}$ | benzenesulphonates | » | [256] |
| naphthalenesulphonates | » | naphthalenesulphonates | » | [238] |
| hydroxynaphthalenesulphonates | » | hydroxynaphthalenesulphonates | » | [257] |
| aminonaphthalenesulphonates | » | aminonaphthalenesulphonates | » | [259] |
| anthraquinonesulphonates | » | anthraquinonesulphonates | » | [260] |
| alkyl sulphonates | » | alkyl sulphonates | » | [261] |
| alkyl sulphates | » | alkyl sulphates | » | [44] |

*For notation see Table 1; emis = atomic emission, at.abs = atomic absorption, ph.titr = photometric titration.

acridine in compounds with $TeBr_6^{2-}$ [134] can then be regarded as proof of outer-sphere association.

The irregular distribution of electron density in dye cations,[3,165,168] which influences the stability of the corresponding OC by non-Coulombic interaction,[85,152] apparently opens up the possibility of a search for the optimum outer-sphere cations for use in the determination of metals as OC based on acido-complexes. For example, in the extraction-photometric determination of lead, best results were obtained using OC formed by the halogeno-complexes of this element with Brilliant Green and Malachite Green ($PbCl_3^-$) or Victoria Blue 4R ($PbBr_3^-$).[156] Examples of increase in the complexity of the outer-sphere species of OC used as analytical forms are provided by the compounds of $BiI_4^-$ with the phenylhydrazone-1,3,3'-trimethyl-2-formylindolinium cation,[164] of $SbCl_6^-$ with Phenosafrazo Blue,[165] and other compounds.[141]

The anionic coordinating centre of OC, in addition to acido-ligands, may sometimes also contain other species contributing to its coordination saturation. Examples of such systems are the OC of $AuCl_3(OH)^-$ with Chromopyrazole,[158] of $SbCl_5(OH)^-$ with the cations of triarylmethane dyes,[3] of $PdX_3(H_2O)^-$ (X = $SCN^-$, $I^-$, $Br^-$, $Cl^-$) with the cation of Brilliant Green,[155] and of $PbX_3^-$.Solv (X = $Cl^-$, $Br^-$; Solv = benzene, toluene, pentyl acetate) with the cations of triphenylmethane dyes.[156] The OC of $AlF_2F_2^{3-}$ (R = Xylenol Orange) with tri-n-octylamine has been used for the extraction-photometric determination of fluorine.[169]

The difference in the stabilities of labile OC makes exchange of outer-sphere species possible. For example, exchange between the cation of Crystal Violet in its OC with $SbCl_6^-$ and the cations of antipyrine, diantipyrinylmethane, and its analogues, and also trioctylamine, has been used for their determination.[13]

An original type of coloured OC is represented by the compounds of anionic complexes of elements with organic reagents and with the outer-sphere cations of surface-active substances (SAS). In this case a marked improvement in the analytical characteristics of the reactions in aqueous solution is achieved by the complex effects of hydrophobic interaction.[170,171] The outer-sphere complexes formed by the anionic compounds of disulphodecylfluorene with molybdenum(VI), tungsten(VI), germanium, titanium(IV), and tin(IV) with outer-sphere cations of the N-cetylpyridinium type have been characterised as outer-sphere chelates.[172] The sensitivity and selectivity of the reactions in these systems are much better than in those examined above. For example, in nickel and its alloys it is possible to determine $3 \times 10^{-5}$% antimony as the OC of its trihydroxyfluoronate with the N-cetylpyridinium cation in the outer sphere.[173]

The stability of OC towards ultraviolet radiation has not been specially studied, but the ability of iron(III) as $[Fe(phen)_3X_n]$ (X = $ClO_4^-$, $C_2O_4^{2-}$) to undergo photochemical reduction has been used for its determination.[48] The photometric study of mercury-catalysed ligand exchange in $Fe(CN)_6^{4-}$ to give OC based on iron(II)–phenanthroline complexes has made it possible to determine down to 200 ng $ml^{-1}$ of the catalyst element.[29]

Examples of the use of OC in photometry and fluorimetry[174–185] are given in Table 2.

## 4. Outer-Sphere Complexes in Extraction

The extraction of OC is used to isolate or separate elements and in mixed methods of analysis. In general it is possible to draw a parallel between the coordinative unsaturation of the compound extracted, the necessity of which is one of the basic postulates of extraction theory,[186] and the state of the metal ion in the coordinating centre of the OC, when the inner-sphere ligand occupies the energy gap between the central atom and the outer-sphere ligand. This makes it possible to formally compare the properties of the OC being considered in this section with the properties of other extractable compounds. The lack of data on the stability of extractable OC towards solvolytic dissociation in polar solvents creates certain difficulties in applying the concepts of outer-sphere coordination in extraction chemistry, but the available experimental data[67] indicate that this approach is promising.

The use of OC in extraction can be examined on the basis of the type of compound transferred to the organic phase[18,30,32] or on the basis of the characteristics of the extraction process.[19] In the first case, the OC may be various coordinatively non-solvated salts, that is compounds of the type $[Fe(phen)_3](ClO_4)_2$, $[Ca(TBP)_m](SCN)_2$, $[Tl(TBP)_3(H_2O)]Cl_4$ (TBP = tributyl phosphate); compounds of metal solvates, for example $(Mg.Solv)Cl_2$, $(Ca.Solv)(SCN)_2$; and the compounds of acidocomplexes with organic cations, examined above.[18,30,32] The significant covalent contribution to the chemical bond in the outer sphere is revealed by the anomalously high distribution coefficients, as for example in the extraction of tetrachlorogallate by 2-octylaminopyridine.[67] Many extractable compounds of anionic complexes of metals—halide and thiocyanate,[13,14,18,19,187] less frequently nitrate,[20] carbonate,[188] and others[14,110,113]—with the cations of organic bases, of considerable importance in analytical chemistry, are apparently OC.

In the second case it is possible to consider from the viewpoint of outer-sphere complex formation the processes involved in the cation- and anion-exchange extraction of cationic and anionic inner-sphere coordinatively saturated complexes respectively.[19] The outer-sphere coordination of the molecules of organic solvents by neutral metal chelates, distinguished by its orientational specificity and discrete character,[11] makes it possible to relate their extraction, and also the forms of various adducts used in analytical chemistry,[3] to these phenomena.

Synergic extraction in various systems can also be related to the formation of OC. Thus the formation of stable adducts, essentially OC, observed in the extraction of europium by thenoyltrifluoroacetone in the presence of quinolinium cations in cyclohexane, benzene, carbon tetrachloride, and chloroform, increased the extraction constant by a factor of about $10^5$.[189] The formation of a compound containing the inner-sphere complex of uranyl ions with di-(2-ethylhexyl) phosphate and a molecule of a crown ether in the outer sphere made possible the synergic extraction of the element into nitrobenzene.[190]

Competing processes in the outer sphere can explain the suppression, usually interpreted in terms of the "common ion" mechanism, of the extraction of indium from bromide solutions containing the cations of Brilliant Green into benzene in the presence of thallium(III), or the decrease in the extraction of thallium(III) from chloride solutions into chloroform with Crystal Violet in the presence of mercury.[191]

The extraction of OC is used for the effective separation of elements,[30,32,192] including platinum metays with similar properties.[193,194] Various analytical methods are used to determine the elements after their separation or extraction, for example titrimetric (after the separation of zinc and cadmium by extraction from halide solutions by dipyrazolonylmethane[195]), atomic emission (after the extraction of gold(III) and thallium(III) by Chlorex[196]), flameless atomic absorption (in the determination of thallium(III) in sedimentary rocks[197]), and radiometrically (after concentrating iridium and rhodium

by 2-octylaminopyridine,[198] thallium(III) by alkyldiamines,[199] and other elements by methyltrioctylammonium chloride[200]). Small quantities of silver can be determined by an extraction-catalytic method based on the catalytic oxidation of Bromopyrogallol Red (BPR) by persulphate in the presence of 1,10-phenanthroline and extraction of the catalyst [Ag.$(phen)_2$]BPR by nitrobenzene.[29] Examples of the use of OC in extraction[49,195–202] are given in Table 2.

### 5. Outer-Sphere Complexes in Ionometry

The properties of various OC correspond effectively to the requirements to be satisfied by electrode-active materials in membrane liquid ion-selective electrodes (ISE). These requirements include low solubility in water, ready extractability into an organic solvent, ensuring that the OC is in the membrane phase of the liquid ISE, and the ability of the OC to undergo selective ionisation in the outer sphere, resulting from the low activation energy of this process.

These properties are shown by, for example, the OC, dissolved in nitrobenzene, of the phenanthroline complexes of iron(II), nickel, and various other metals with different anionic outer-sphere ligands. Depending on the nature of the outer-sphere ligand, it is possible to prepare ISE for determining $NO_3^-$, $BF_4^-$, $ClO_3^-$, $ClO_4^-$, $IO_4^-$, $ReO_4^-$, and various other anions.[21–24] Since the rate of exchange of a transition metal on a membrane surface is much lower than the rate of anion exchange, the potential of the ISE is determined by the activity of the corresponding outer-sphere ions in the solution. The selectivity of ISE of this type generally decreases in the order $PF_6^- > ClO_4^- > SCN^- > I^- > BF_4^- > NO_3^- > Br^- > Cl^-$, and this can be related to the change in the stability of the OC.[21] A large number of examples of ISE with membranes containing compounds of this type have been described.[203–206]

Electrode-active properties are shown by solutions of the dimethylphenanthroline complex of copper(I) with sulphate and picrate ions in the outer sphere in dibutyl phthalate. This made it possible to develop ISE for the determination of these cationic complexes of copper(I).[24,207] Similar properties are shown by solutions of OC based on thiourea complexes of silver and gold(I) in nitrobenzene, chlorobenzene, and 1,2-dichloroethane.[24,206,208] An electrode with a membrane based on a silver complex can also show an electrode function with respect to phosphate ions.[203]

Electrode-active properties are shown by various OC of anionic halide and pseudohalide complexes of metals with different organic anions in the outer sphere, capable of undergoing solvolytic dissociation in polar organic solvents such as *o*-dichlorobenzene, decan-1-ol, etc.[21,24,204,209–216] ISE of this type are used in flow injection methods in automatic chemical analysis.[46,47]

Additional information on the use of OC with different coordinating centres as electrode-active substances in membrane liquid ISE are given in Table 2.

### 6. Outer-sphere Complexes in Chromatography

The low activation energy of the replacement of outer-sphere ligands in OC makes it possible to carry out this process under the dynamic conditions of various forms of liquid chromatography with extensive repetition of sorption and desorption processes in new layers of sorbent. In different specific cases the stationary phase may be associated either with the coordinating centre of the OC (inner-sphere complex) or with the outer-sphere ligand. The concepts of outer-sphere coordination can be used in ion-exchange, ligand-exchange, and extraction chromatography and in the liquid chromatography of coordinatively saturated metal chelates. The possibility of carrying out "fine" separations of mixtures of substances and concentrating elements is of practical importance. An infrared spectroscopic study of the characteristic features of cation-exchange resins with sulphonate functional groups showed that during ion-exchange sorption on a sulphonic acid cation exchange resin, characteristic OC of the metal aquo-ions with the solid polyelectrolyte in the outer sphere are formed.[217] The formation of OC is also the first stage of the exchange of metal ions in complex-forming ion exchangers.[28] The anion exchange of halide, pseudohalide, nitrate, and other complexes of various metals on anion exchange resins involves the formation of OC.[218,219] In this case the anionic complexes react with the cationic groups of the quaternary ammonium bases of the ion exchange resin, that is with outer-sphere species fixed in the stationary phase. Ion-exchange processes have proved to be effective for the group concentration of micro-quantities of transition metals[220] as their phenanthroline complexes on a polyfunctional outer-sphere ligand (KU-2 cation exchange resin), and is also a convenient method for separating the phenanthroline complexes of nickel, iron(II), and ruthenium(II) on modified silica.[221]

The difference in the stability of OC based on $[Co(en)_3]^{3+}$ with anionic ligands leads to differences in their retention times in the anion exchanger phase, and this has made it possible to separate mixtures of oxalates and sulphates[222] and fumarate and maleate ions.[223]

An even finer chromatographic separation can be achieved by the highly selective method of ligand-exchange chromatography, based on outer-sphere ligand exchange.[25] This makes it possible to separate mixtures of compounds with very similar properties, for example the optical isomers of kinetically inert complexes of chromium(III) and cobalt(III) and various other metals by chromatography on dissymmetric sorbents, or racemates of the tris(oxalato)-compounds of cobalt(III) and chromium(III) as their OC with the cations of brucine, quinine, or cinchonine by electrophoresis.[25] Optically active metal complexes can be used for the enantioselective coordination of asymmetric species in the outer sphere, and this makes it possible, for example on silica gel modified by N-aminoethylaminopropyl groups and Λ-(+)-$[Co(en)_2(NO_2)_2]^+$, to separate respectively the racemates of organic acids and the tris(oxalato)-compounds of cobalt(III) and chromium(III).[224] The modification of silica gel by chloroamine complexes of cobalt(III) makes possible the chromatographic separation of dinucleotides and cephalosporins.[225] The stereoselectivity of outer-sphere complex formation on Sephadex A-25 has been used to separate the racemates of (glycinato)bis(oxalato)cobaltates(III).[69]

The concepts of outer-sphere coordination are actively used in the interpretation of the mechanism of the separation of neutral coordinatively saturated metal chelates by liquid adsorption chromatography in chloroform, di-isopropyl ether, and other solvents with medium polarity.[26,27,89,226–229] The chromatographic properties of the chelates of metals with acetylacetone, benzoylacetone, dibenzoylmethane, dibutyldithiophosphinate, and other multidentate ligands depend on the structure of the ligand fragment peripheral to the chelate unit. The difference in the mobility of these chelates is attributed to the formation of hydrogen bonds between a peripheral electronegative atom of the ligand and the surface

hydroxide groups of the sorbent,[26,27] that is outer-sphere coordination.

Since in organic solvents neutral metal chelates are present as OC,[11] the chromatographic process being considered can be regarded as a characteristic ligand exchange of the outer-sphere molecules of organic solvents with the surface groups of the sorbent.

The concepts of OC formation can also be used in the extraction chromatography of anionic metal complexes,[90,230] as in the case of anion-exchange extraction.[19] The formation of outer-sphere compounds of anionic chloro-complexes of iron(III), copper, cobalt, and other elements in the trioctylamine in toluene—Fluoroplast system has made possible the selective concentration of micro-quantities of these elements. They were determined with a detection limit of $10^{-6}$–$2 \times 10^{-5}$% by flame atomic absorption or emission spectroscopy.[231] The use of high-pressure liquid chromatography for complex analytical purposes has been examined.[232]

## 7. Outer-Sphere Complexes in Organic Analysis

The electron-donor or electron-acceptor properties of the molecules or ions of organic compounds make it possible to attach them as outer-sphere species to coordinatively saturated metal complexes to give OC used as analytical forms. Since the organic compounds considered here have an anionic or cationic function in solution, the pH must be selected to obtain OC. For analytical purposes, use is generally made of the low solubility of OC in water, or their ability to be extracted into an organic solvent. The actual determination is carried out by titrimetric, photometric, atomic absorption, radiometric, and other methods. An example is the determination of aliphatic and aromatic sulphonates.[233]

The outer-sphere compounds of iron(II) chelates with heterocyclic diamines and alkyl sulphates have been used for the sensitive determination of small quantities of these outer-sphere anions.[234] Even greater sensitivity and variety are shown by methods for the extraction-atomic absorption determination of organic substances with an anionic function, such as sulphonates, aminoacids, carboxylic acids, antibiotics, and other compounds from the atomic absorption by copper(II), cobalt(II), cadmium, and nickel[35] in the coordinating centre of the OC.

Various organic compounds with a cationic function can be determined as OC containing anionic inner-sphere metal complexes. OC of this kind are formed in the detection of xanthene dyes by precipitating their cations with $SbCl_6^-$, $AuBr_4^-$, and other anionic complexes; in the detection by extraction of higher aliphatic acids in paraffin wax and vaseline from the formation of coloured compounds of $[UO_2(RCOO)_3]^-$ with the cations of basic dyes;[235] and in the identification of biotin by the reaction with $PtI_6^{2-}$, of thiamine and Vitamin B with $HgCl_4^{2-}$, of the hexamethonium cation with $CdI_4^{2-}$ and other similar compounds.[33] The low solubility of complexes of $[Cr(SCN)_4(NH_3)_2]^-$ with outer-sphere cations has been used to detect pyridostigmine and carbocholine,[33] and also in the photometric determination of aniline, betaine, brucine, caffeine, morphine, pilocarpine, and other compounds as the corresponding OC, dissolved in acetone after precipitation and filtration.[34] It is more convenient to carry out the extraction-photometric determination of various amines as their OC with $Co(SCN)_4^{2-}$.[34] The quantitative determination of alkaloids, aminoquinoline, cationic surfactants, and other organic compounds of similar character by atomic absorption after extraction of their OC with Reinecke's salt or $Co(SCN)_4^{2-}$ appears promising.[35]

In some specific cases the method of analysis in the final stage may be simpler, for example titrimetry in the determination of thiamine as its OC with $BiI_4^-$.[236] The outer-sphere coordination of alcohols by vanadium(V) 8-quinolinolate in chloroform or benzene has been used for their photometric determination.[34] Down to 2 μg of albumin can be determined by making use of its ability to lower the catalytic activity of $[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3$ in the chemiluminescent reaction of luminol with hydrogen peroxide.[237]

## 8. Outer-Sphere Complexes in Aqueous-Organic Solutions

Aqueous-organic solvents are binary systems which have complex compositions and in which the influence on the solute is complex.[56] In aqueous-organic solutions, metal aquo-ions can hold various outer-sphere ligands more firmly than in water, as a result of hydrogen bonding, and this is of considerable importance for analytical practice.[39,40,44,238,239] In some cases the selection of the metal aquo-ions acting as the coordinating centre of the OC can be based on the concept of localised hydrolysis.[44,238,239] From general considerations,[8] superposition of the effects of outer-sphere and inner-sphere coordination is possible in this case, but this does not influence the analytical results achieved.

The formation of outer-sphere complexes by metal aquo-ions with anionic ligands in aqueous-organic solutions is used to mask interfering reactions, in the indirect photometric determination of sulphates,[239] sulphites, and hydrogen phosphates,[240] and, most effectively, in indicator spectrophotometric titration.[42,241,242]

The masking of the reaction of barium with bis(azo)-derivatives of chromotropic acid as a result of the formation of stable OC $[Ba(OH_2)_6]SO_4$ [239] in aqueous acetone and aqueous ethanol solutions can be used to improve the selectivity of the photometric determination of the alkaline earth metals.[243] The same method is used to mask barium in the photometric determination of strontium in barium salts.[244] The formation of OC of this type is particular widely used in methods for the indirect photometric determination of sulphates,[245,246] in their spectrophotometric titration,[247–249] and also in the indicator spectrophotometric titration of mixtures of microgram quantities of barium and strontium.[250] The high rate of formation of these OC makes the corresponding reactions suitable for the sensitive automatic determination of sulphates. The productivity of this analysis reaches 60 specimens per hour,[45] and the information efficiency is very high, 433 byte $h^{-1}$.[239]

Outer-sphere complexes of similar type, formed by barium aquo-ions in aqueous-organic solutions, can also apparently contain the structural analogues of sulphate ions—selenate, chromate, molybdate, fluoroberyllate, and other complex anions of elements of groups IV–VI. This makes possible the selective spectrophotometric titration of micro-quantities of these elements by barium salts in aqueous acetone and aqueous acetonitrile solutions.[241,251–255]

The formation of neutral OC by barium aquo-ions with the anions of various aromatic sulphonic acids, aliphatic sulphonates, and sulphates in aqueous acetone solutions opens up extensive possibilities for the determination of organic compounds containing the corresponding functional groups, by indicator spectrophotometric titration with barium salts.[39,42,44] Of particular interest are methods for the selective determination of various sulphonates of the benzene,[256] naphthalene,[238,257–259] and anthraquinone[260] series, which also make it possible to analyse mixtures of sulphates with any sulphonates, and the mixtures of isomeric products obtained in industrial processes, and this is of considerable

practical importance.[42] Sensitivity and selectivity are also shown by similar methods for determining alkyl and alkylaryl sulphonates and alkyl sulphates,[261,262] and also substances containing a thiol group, for example cystine, cysteine, Captax, and others, after their oxidation to sulphonates by hydrogen peroxide in an alkaline medium.[263] Aromatic sulphonates can be titrated without interference from sulphate ions using solutions of potassium salts in aqueous acetone,[264] where the formation of neutral OC by aquo-ions of potassium with the sulphonates is possible. The aquo-ions of other alkaline earth metals can be used to determine alkyl phosphates, aryl arsenates, and carboxylates by this method.[265]

The solvated potassium ion can undergo outer-sphere coordination with various polyatomic and complex anions in aqueous dimethyl sulphoxide solutions.[40,43,266] This has been shown by spectroscopic and polarographic studies of fluorocomplexes of group V elements.[41] In general, the formation of OC of this type is related to the characteristic features of the behaviour of the dimethyl sulphoxide molecule in the solvate layer of the potassium ion. The coordination of the dimethyl sulphoxide molecule to metal ions through the oxygen atom leads to an increase in the strength of the $S^+ \rightarrow O^-$ $\sigma$-bond and to slight polarisation of this bond. This increases the ability of the coordinated dimethyl sulphoxide molecules to undergo ion–dipole interaction with outer-sphere anionic ligands, and leads to the formation of relatively stable outer-sphere associates, suitable for titrimetric determinations.

The materials determined by spectrophotometric titration with potassium salts in aqueous dimethyl sulphoxide solutions are outer-sphere ligands consisting of the anionic fluorocomplexes of the elements of groups III,[266,268–270] IV,[271] and V[41,272–274] of the periodic system, perrhenates,[275] chlorates, perchlorates,[276] chloro-complexes of palladium(II), platinum(IV),[43,277] and ruthenium(IV),[267] and other polyatomic anions.[242]

The methods developed are highly selective in the analysis of mixtures of elements with similar properties, for example tantalum and niobium,[272,273] uranium and thorium,[270] and palladium and platinum,[43,277] for the determination of chlorates and perchlorates,[276] and in other cases.[242] The absence of interference from hydrolysis, hydrolytic polymerisation, and masking reagents makes these methods convenient in practice. These methods have found practical application in the analysis of minerals,[254] glasses,[253] alloys,[43,268,271] fertilisers,[269] electroplating bath electrolytes,[266] and other materials.[248,274]

The use of OC formation in spectrophotometric titration is illustrated in Table 2.

## IV. SUMMARY

The material presented indicates the intensive development of the application of OC in various fields of present-day analytical chemistry, associated with their flexibility and variety in the production of appropriate analytical signals. The achievements have been most significant in the development of new sensitive and selective methods of analysis associated with the direct use of OC or the reactions involved in their formation. Examples are provided by interesting applications in analytical concentration, extraction-photometric and extraction-fluorimetric methods, ionometry, titrimetry in aqueous organic solutions, and ligand-exchange chromatography. The further development of the analytical applications of OC should lead to new methods for determining elements and organic compounds, showing a high selectivity combined with the necessary sensitivity. These may be, for example, original photometric and fluorimetric methods, ion-selective electrodes for doubly-charged anionic complexes of elements and organic ionophores, methods for the spectrophotometric titration of elements as anionic pseudohalide complexes, "fine" effects of separation in ligand-exchange chromatography, and new methods for the automatic analysis of solutions.

A characteristic feature of the present state of the analytical chemistry of OC is the practical absence of, and hence urgent need for, quantitative data on the stability of these compounds; this is to a considerable extent preventing the possible achievement of maximum pragmatic effects in the development of new methods. The problem of estimating the contribution of outer-sphere interaction to complex-formation equilibrium in labile analytical systems, particularly in aqueous-organic solutions, is most complex. Further studies in this field should apparently find an adequate solution.

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# Polyiodo-iodates Containing Five or More Iodine Atoms

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The results of theoretical and experimental studies of the chemistry of polyiodo-iodates—complexes of iodine containing five or more iodine atoms in the anion—have been reviewed. The molecules of heterocyclic compounds with a planar configuration, chelates of *d* elements with macrocyclic planar ligands, and organic and inorganic polymers containing cavities and channels, on oxidation with iodine, tend to form compounds with polymeric anions in the form of quasi-one-dimensional chains. New ideas on iodine as a complex-forming species have been examined.
The bibliography contains 222 references.

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## I. INTRODUCTION

Polyiodo-iodates containing five or more iodine atoms not only may be discrete, $[I_5]^-$, $[I_7]^-$, $[I_9]^-$, and $[I_8]^-$ but also may form chains containing as units the anions $[I_3]^-$ and $[I_5]^-$.[1-7] The study of the correlation between the interatomic distances and valence angles in polyiodo-iodate anions, and the analysis of vibrational and rotational spectroscopic data, indicate that there is a genetic relationship between the structures of these anions and the structure of the $[I_3]^-$ anion.[4,6] Aqueous and non-aqueous solutions contain chiefly anions with composition $[I_3]^-$, whose formation constants have been determined fairly accurately. The formation of $[I_5]^-$ anions in non-aqueous solutions has been assumed. The existence in solution of hepta-iodide and nona-iodide anions and anions with a chain structure has not been reliably established, however. These anions are apparently formed in the layer next to the surface in a crystallising substance during the establishment of the most stable structures, involving repeated transfer of the cations and anions from lattice sites to the solution and back again. The stability of the anions decreases from $[I_5]^-$ to $[I_9]^-$, the external conditions remaining constant.[8] Polyiodo-iodate anions readily undergo changes in structure and composition under the influence of even slight changes in the environment.

Subsequent sections examine present-day ideas on the nature of polyiodo-iodate anions.

## II. PENTA-IODIDES

Penta-iodides contain the $[I_5]^-$ anion.[1] An anion with this composition has been detected in tetra-alkylammonium[9-15] and quinuclidine[16] compounds, in the iron complexes $[Fe(Et_2S_2.CN)_3][I_5]$,[17] $\{[Fe(C_5H_5)(C_5H_4)]_2Se\}[I_5]$,[18] and $[Fe(C_{10}H_9)].[I_5]$,[19] and in various ammines[20-22] and ethylenediamine complexes,[23] although in the last two groups of compound the composition of the anion was established only by chemical analysis, and not always qualitatively.[20-23]

A study[3] of the reaction of dithizone with molecular iodine showed that the crystal structure of the polyiodo-iodate formed contains dimers with the composition $[(\text{dithizone})I]^+-[I_5]^--I_2-[I_5]^-[(\text{dithizone})I]^+$ with an angular (85.5°) $[I_5]^-$ anion.

In all the systems, studied up to the present, of the type $MI-I_2$ and $MI-I_2$–solvent at 0–25 °C (M = K, Rb, or Cs), an $M[I_5]$ phase was not detected.[24-31] A very small region corresponding to the crystallisation of the incongruently melting (+9.8 °C) $(NH_4)[I_5]$ was detected only in the $NH_4I-I_2-H_2O$ system at 0 °C.[32] In the systems $(NR_4)I-I_2-C_6H_6$ (or $C_6H_6CH_3$) at 6 °C and 25 °C, the phase $(NMe_4)[I_5]$ is formed.[33] This compound also crystallises in the $(NMe_4)I-I_2$ system.[34]

The evidence[35] for the possible formation of the incongruently melting compounds with the composition $[M(NH_3)_4][I_5]_2$ (M = Zn or Cd) in $[M(NH_3)_4]I_2-I_2$ system is not unambiguous.[4] The logarithms of the formation constants (lg β) of the $[I_5]^-$ anion in the reaction:

$$[I_3]^- + I_2 \rightleftarrows [I_5]^-$$

for different solvents at 25 °C and activity coefficients of the components of the system close to 1 were: $H_2O$ 0.95,[36] $C_2H_5OH$ 1.8,[37,38] $CH_3NO_2$ 1.51, $C_6H_5NO_2$ 2.3–2.8,[8,39] propylene carbonate 1.9.[40] The temperature dependence ($t$ in °C) $\lg \beta = 0.954 + 0.0308(t - 25)$ for aqueous solutions gives for this reaction the values $\Delta G^0_T = -5.4$ kJ mole$^{-1}$ and $\Delta H^0_T = 50.1$ kJ mole$^{-1}$.[36] The thermodynamic characteristics of the reaction

$$(NMe_4)[I_3]\,(\text{crystalline}) + I_2(\text{crystalline}) = (NMe_4)[I_5]$$

are: $\Delta G^0_{298} = -13.4 \pm 0.03$ kJ mole$^{-1}$, $\Delta H^0_{298} = -9.2 \pm 0.4$ kJ mole$^{-1}$, $\Delta S^0_{298} = 13.4 \pm 1.7$ kJ mole$^{-1}$ K$^{-1}$.[41]

The structure of the bis(di-iodine)iodate(−1) anion $[I_5]^-$ is given in Fig.1. The anion has an almost planar (±0.12 Å) *V*-shaped configuration with an angle of 88.2–96.5°. The complex-forming species in the anion is the $I^-$ ion, and the ligands are polarised iodine molecules with an interatomic distance of 2.75–2.93 Å. The $I^--I_2$ bond is weak, and its length is 3.01–3.31 Å.[3,16,17,42-46] The force constant of the

vibrations of the complex-forming species is low ($0.15 \times 10^5$ dyne $cm^{-1}$), and the ion is readily deformed in an unsymmetrical crystal field, forming chain and cyclic structures (Fig.2).[3,16,18,44,45,47]

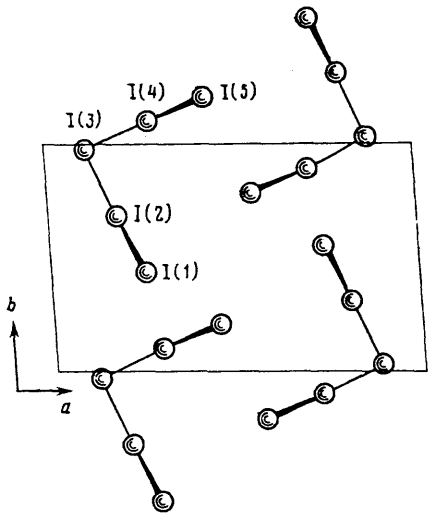



**Figure 1.** Projection of the $[I_5]^-$ anions of the compound $[Fe(Et_2S_2CN)_3][I_5]$ on the *ab* plane:[17] angles: I(1)–I(2)–I(3) = 176.2°; I(2)–I(3)–I(4) = 88.2°; interatomic distances (Å): I(1)–I(2) = 2.799; I(2)–I(3) = 3.148; I(3)–I(4) = 3.015; I(4)–I(5) = 2.837.

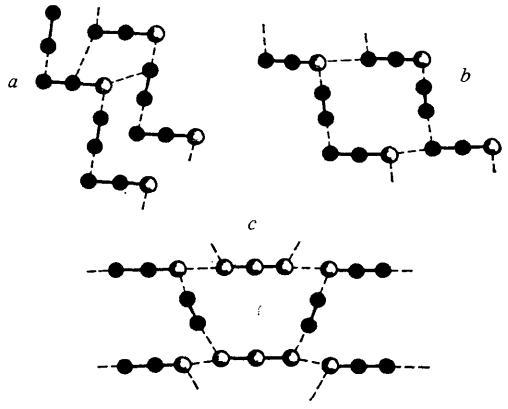



**Figure 2.** Schematic representation of the polyiodo-iodates in various bis(di-iodine)iodates:[18,44] *a*) [(phenacetin)$_2$H][$I_5$]; *b*) [bis(ferrocenyl)selenium][$I_5$].0.5$CH_2Cl_2$; *c*) [(quinuclidine)H][$I_5$]; the black circles denote the iodine atoms of the coordinated iodine molecules.

A calculation[48] of the energies of formation of the $[I_5]^-$ anion in the reaction

$$I^- + 2I_2 = [I_5]^-$$

confirmed its *V*-shaped configuration. The energy for this structure is lower than the energies of formation of the linear, square-planar, and *T*-shaped configurations.

The chemical shifts in the $[I_5]^-$ anion have been examined in terms of six-electron MO, of which the three MO of lowest energy (two bonding and one non-bonding) are completely occupied by electrons. The complex-forming species has an effective charge of −0.5e, and the terminal atoms of the ligands from −0.13e to −0.26e. The iodine atoms directly attached to the complex-forming atom, however, carry positive charges of from 0.08e to 0.11e (from different calculations).[49]

The existence of the $[I_5]^-$ anion as a structural unit is confirmed by data obtained by vibrational spectroscopy,[14] analysis of the nuclear quadrupole resonance spectra,[50] Mössbauer spectroscopy,[51] and X-ray spectroscopy.[52]

The electronic spectra of solutions of compounds containing $[I_5]^-$ anions in acetonitrile and 1,2-dichloroethane ($\lambda_{max}$ = 295 nm, lg ε = 4.65–4.68 and $\lambda_{max}$ = 365 nm, lg ε = 4.40 to 4.42 respectively[10,15]) are identical to those of polyiodo-iodates containing the anions $[I_3]^-$, $[I_7]^-$, and $[I_9]^-$.

The existence of $[I_6]^{2-}$ anions in aqueous solutions[36] and of $[I_6]^-$ anions in the crystalline phase[19] is unlikely.

## III. HEPTA-IODIDES

Hepta-iodides contain the $[I_7]^-$ anion.[1] This anion has been detected in tetra-alkylammonium polyiodo-iodates[14,15,53,54] and various ammines,[20–22] and in dilute solutions containing iodine and lanthanide iodides in molar ratios close to $I^- : 3I_2$.[55,56] Unfortunately, in almost all the works cited the compositions of the bis(di-iodine)tri-iodates obtained by preparative methods were established only from an incomplete chemical analysis, and the formation of the $[I_7]^-$ anion in solution was established using the spectrophotometric version of the Ostromyslenskii–Job method, not applicable in this case.

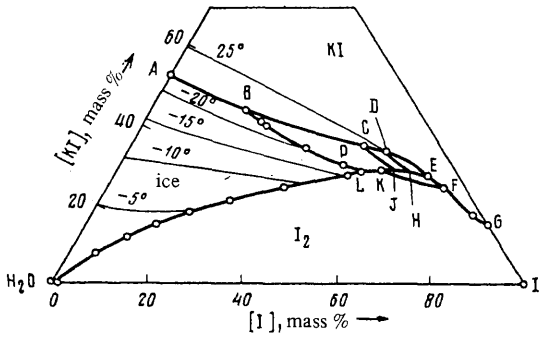



**Figure 3.** Triangular projection of the polythermal equilibrium diagram of the KI–$I_2$–$H_2O$ system;[25] crystallisation fields: K[$I_3$].$H_2O$—DEHD; K[$I_7$].$H_2O$—KJHEFK; α-K[$I_3$].2$H_2O$—BCJKLPB; β-K[$I_3$].2$H_2O$—CDHJC.

The results obtained in a study of a number of systems in which the formation of bis(di-iodine)tri-iodates has been detected are contradictory. Thus in the purely eutectic KI–$I_2$ system, the formation of K[$I_7$] was established erroneously[29] (because of poor experimental technique, part of

the solidus line was taken as an extremely flat liquidus curve). A number of papers describe the study of $KI-I_2-H_2O$ systems,[24,25,27,29–31,57] but the only apparently reliable data are those in Refs.25, 31, and 57 on the existence of $K[I_7].H_2O$ (Fig.3), although in this case also the individuality of the new phases was not confirmed by chemical methods of analysis.

Studies of $MI-I_2-C_6H_6$ systems (6 °C and 25 °C, M = K or Rb) have shown that phases containing the $[I_7]^-$ anion always crystallise as the following solvates, which decompose readily in air: $K[I_7].2C_6H_6$,[29,57] $Rb[I_7].4C_6H_6$, and $Rb[I_7].2C_6H_6$ (Fig.4). This apparently explains the contradictory conclusions regarding the existence of the solvate $K[I_7].2C_6H_6$.[26,28,29,33,57] Compounds containing the $[I_7]^-$ anion were not detected in the systems containing CsI.[28,58] The reasons for the non-existence of regions corresponding to the crystallisation of the phases $M[I_5].xC_6H_6$ (M = Rb or Cs) in the above systems, and the appearance of the non-solvated phase $Cs_2[I_8]$ when RbI is replaced by CsI, have not yet been established.

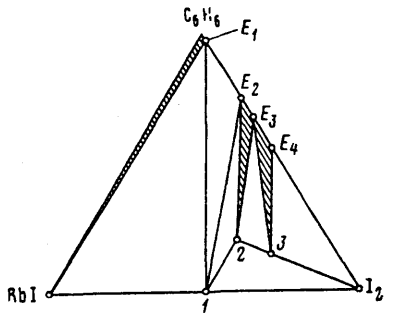



Figure 4. Equilibrium diagram of the $RbI-I_2-C_6H_6$ system, 25 °C:[28] *1*) $Rb[I_3]$; *2*) $Rb[I_7].2C_6H_6$; *3*) $Rb[I_9].2C_6H_6$; compositions of the eutonic points ($I_2$, M): $E_1 = 0.01325$; $E_2 = 0.3425$; $E_3 = 0.393$; $E_4 = 0.545$.

The structure of the $[I_7]^-$ anion is given in Fig.5.[53] The $[I_7]^-$ anion can be represented as the bis(di-iodine)tri-iodate ion $[(I_3)(I_2)_2]^-$, in which the unusual complex-forming species is the symmetrical $[I_3]^-$ anion, to which are coordinated two iodine molecules, which are situated at equal distances (3.43 Å) from the terminal atoms of the central ion and which are weakly bonded to it.[59] The $[I_3]^- - I_2$ distance is slightly less than $I_2-I_2$ distance in crystalline iodine (3.56 Å). The structure of polymeric polyiodo-iodate anions is beginning to form in this anion. The thermodynamic characteristics of the reaction

$$(NEt_4)[I_3]\,(\text{crystalline}) + 2I_2 = (NEt_4)[I_7]\,(\text{crystalline})$$

are $\Delta G^0_{298} = -22.0 \pm 0.6$ kJ mole$^{-1}$, $\Delta H^0_{298} = -23 \pm 1.2$ kJ mole$^{-1}$, and $\Delta S^0_{298} = -3.8 \pm 3$ J mole$^{-1}$ K$^{-1}$.[41]

## IV. OCTA-IODIDES

Octa-iodides are polyiodo-iodates containing the doubly-charged $[I_8]^{2-}$ anion. The following compounds containing this anion have been synthesised: $Cs_2[I_8]$,[28,33,58,60–62] $[(DMX)_2H_2][I_8]$,† [44] $[M(TACD)][I_8]$# (M = Ni, Pd, Pt),[63–65] $[Co(en)_2X_2][I_8]$§ (X = $Cl^-$, $I^-$, $NO_2^-$, and NCS),[66] and $[Ni(en)_3][I_8]$, crystallised from methanol.[67]

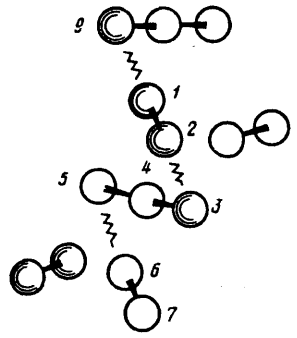



Figure 5. Fragment of the structure of the $[I_7]^-$ anion of the polyiodo-iodate $(NEt_4)[I_7]$ at −175 °C;[53] the hatched iodine atoms are in the same plane; *1*–*7*) iodine atoms in the anion; interatomic distances (Å): I(1)–I(2) = 2.73; I(2)–I(3) = 3.43; I(3)–I(4) = 2.90; I(4)–(I(5) = 2.90; I(5)–I(6) = 3.43; I(6)–I(7) = 2.73.

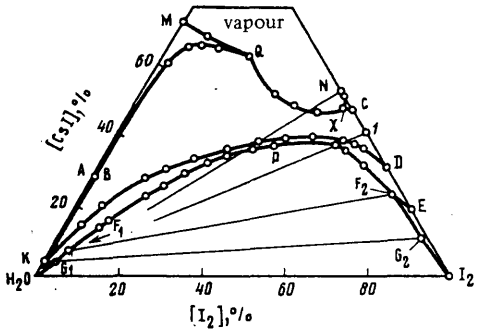



Figure 6. Polythermal equilibrium diagram of the $CsI-I_2-H_2O$ system[62] (pressure 740–750 mmHg, temperature from −5 °C to +305 °C); crystallisation fields: CsI—MQBAM; $I_2$—$EF_2G_2$; $Cs[I_3]$—CXQBKDC; $Cs_2[I_8]$—KDEFPF$_1$K; point N—$Cs[I_3]$; *1*—$Cs_2[I_8]$.

In the $CsI-I_2-H_2O$ system in the temperature range from −5 °C to +305 °C, only two new phases are formed: $Cs[I_3]$ and $Cs_2[I_8]$ (Fig.6). With increase in temperature, the range of crystallisation of the incongruently soluble $Cs_2[I_8]$ decreases, and at 80 °C, a range of separation into layers in the liquid phase appears. The temperature range of the congruent solution of $Cs_2[I_8]$ is very narrow, from 79.5 °C (curve $PF_2$) to 89.0 °C (curve KD). In the range from

† DMX = 3,7-dimethylxanthine.

# TACD = 1,3,5,13-tetra-azocyclohexadecine.

§ en = ethylenediamine.

51.5 °C (isotherm $F_1F_2$) to 79.5 °C (isotherm $PF_2$), $Cs_3[I_8]$ dissolves to give two liquid phases. The field $F_1PF_2$ is the range of the phase equilibrium between $Cs_2[I_8]$ crystals and two liquid phases. According to Ref.68, caesium octa-iodide (but not $Cs[I_5]$) is also formed in the $CsI-I_2$ system (Fig.7), crystallising from the melt below 136 °C. In the $CsI-I_2-C_6H_6(C_6H_5CH_3)$ systems, the largest crystallisation range corresponds to $Cs_2[I_8]$.[28,33,58]

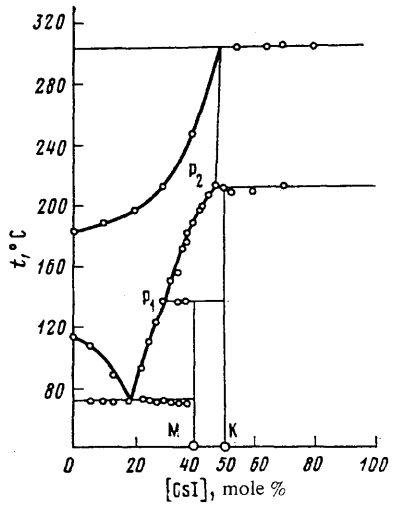



Figure 7. $CsI-I_2$ system (pressure 745 mmHg);[60] coordinates of the point $P_1$: 136 °C (or 141.2 °C [82]) and 30 mole % CsI; M—$Cs_2[I_8]$; K—$Cs[I_3]$.

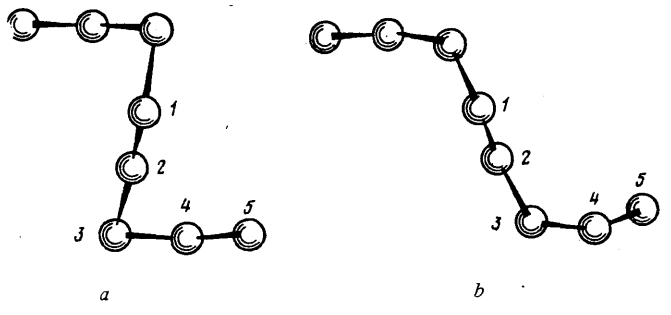



Figure 8. Structure of the $[I_8]^{2-}$ anion;[70,71] *a*) $Cs_2[I_8]$, *b*) $[(CH_2)_6N_4(CH_3)]_2[I_8]$; interatomic distances (Å): *a*) 1–2 = 2.83; 2–3 = 3.42; 3–4 = 3.00; 4–5 = 2.84; *b*) 1–2 = 2.773; 2–3 = 3.386; 3–4 = 3.038; 4–5 = 2.830.

The structure of the $[I_8]^{2-}$ anion is shown in Fig.8. In all polyiodo-iodates studied, the $[I_8]^{2-}$ anion does not have a centre of symmetry and is not planar.[69–71] The complex-forming species in the anion is the strongly polarised iodine molecule, and the ligands are $[I_3]^-$ anions. The $[I_8]^{2-}$ anion is apparently bis(tri-iodido)di-iodate $[(I_2)(I_3)_2]^{2-}$. The representation of the structure of these anions and the separation of their functional parts depend to a large extent on the interpretation of the data on interatomic distances and symmetry. The $[I_8]^{2-}$ anions, when combined with heterocyclic arene cations, can form $[I_{16}]^{4-}$ dimers (Fig.9).[44,63,71] Data on the configurations of polyiodo-iodate anions have been reviewed.[4,72]

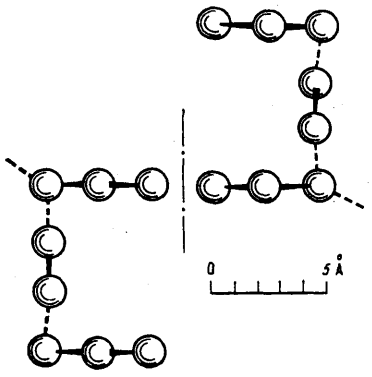



Figure 9. Structure of the $[I_8]^{2-}$ anion in the compound $[(DMX)_2H_2][I_8]$.[44]

The effective charges are +0.08e on the central atoms of the ligands of the $[I_8]^{2-}$ anion, −0.38e on the atoms directly joined to the central iodine molecule, and −0.71e on the terminal atoms.[73,74] Each atom of the central iodine molecule carries a charge of −0.06e.

Studies[75,76] of the thermal stability of $Cs_2[I_8]$ confirmed the results of the structural studies. At 137 °C (or 139° to 140 °C [69]), caesium octa-iodide undergoes incongruent fusion:

$$Cs_2[I_8] \rightarrow \text{melt}\P + Cs[I_3]\,(\text{crystalline}) + I_2(\text{gas})$$

Further heating leads to an increase in the solubility of $Cs[I_3]$ in the melt and hence to a change in the slope of the $\lg p = f(1/T)$ curves, where $p$ is the dissociation pressure, and to the appearance of an inflection at 170 °C. At about 205 °C in the melt, $Cs[I_5]$ decomposes to CsI(crystalline) and iodine. The system after 205 °C is in the same state as in the incongruent fusion of $Cs[I_3]$ (Fig.10), and this explains why the enthalpy changes for the volatilisation of iodine from the two melts practically coincide (46.9 kJ $mole^{-1}$).[75]

The thermal analysis curves for $Cs_2[I_8]$ indicate that the complex decomposes in two stages when heated in air under conditions allowing the free removal of the dissociation products:

$$Cs_2[I_8]\,(\text{crystalline}) = 2Cs[I_3]\,(\text{crystalline}) + I_2(\text{gas})$$

(the start of the inflection on the DTG curve corresponds to 42 °C, and the maximum to 96 °C) and

$$Cs[I_3]\,(\text{crystalline}) = CsI(\text{crystalline}) + I_2(\text{gas})$$

(start of the inflection 107 °C, maximum 158 °C).

---

¶ The melt presumably contains CsI and $I_2$ in the ratio corresponding to the composition $Cs[I_5]$.

Thus the rupture of the chemical bonds in the $[(I_3)-I_2-(I_3)]^{2-}$ anion can take place in two ways: the two bonds may break simultaneously, or only one of them may break to give the ions $[I_5]^-$(liquid) + $[I_3]^-$(crystalline).

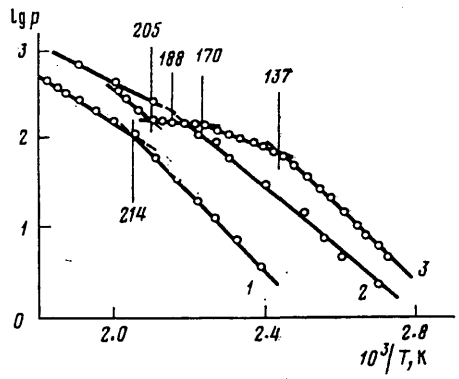



Figure 10. Temperature dependence of the dissociation pressure of polyiodo-iodates:[75,76] *1*) $Cs[I_3]$; *2*) $Rb[I_3]$; *3*) $Cs_2[I_8]$; the temperatures of the phase transformations are given in °C.

The kinetics of the first stage of the thermal dissociation of $Cs_2[I_8]$ in air, described by the equations $dm/d\sigma = km^n$ and $k = Z_0 \exp(-E/RT)$, where $m$ is the mass of the specimen, $\tau$ the time, $k$ the reaction rate constant, $n$ the order of the reaction, $E$ the apparent activation energy, and $Z_0$ the pre-exponential term, are characterised by the quantities $E = 79.1 \pm 1.2$ kJ mole$^{-1}$, $Z_0 = (1.3 \pm 0.4) \times 10^{11}$ min$^{-1}$, $\lg k = 11.114 - 4130/T$ (for $n = 1$).[77,78] Thus the rate of the thermal dissociation is determined by the rate of the diffusion of iodine through the interface. Increase in the decomposition temperature displaces the process into the kinetic range ($n \geq 1$). The dependence of the frequency factor $Z$ on the order of the reaction is given by the equation $Z = Z_0 m_0^{1-n}$, where $Z_0$ is the frequency factor for $n = 1$, and $m_0$ the original number of moles of $Cs_2[I_8]$.

The thermodynamic characteristics of the reaction

$$Cs_2[I_8]\text{(crystalline)} = 2Cs[I_3]\text{(crystalline)} + I_2\text{(crystalline)}$$

are: $\Delta G^0_{298} = 2.6$ kJ mole$^{-1}$, $\Delta H^0_{298} = 3.3$ kJ mole$^{-1}$, and $\Delta S^0_{298} = 2.5$ kJ mole$^{-1}$ K$^{-1}$.[79]

## V. NONA-IODIDES

Nona-iodides are polyiodo-iodates containing the $[I_9]^-$ anion. The appearance of phases with this anion has been established only in the study of non-aqueous systems: $(NMe_4)I-I_2-C_6H_6(C_6H_5CH_3)$ at 6 °C and 25 °C [33] and $MI-I_2-C_6H_6$, where M = K, Rb, or Cs at 25 °C [26,28,29] (the phases $K[I_9].3C_6H_6$, $Rb[I_9].2C_6H_6$, and $2Cs(I_9].3C_6H_6$). In the opinion of Popov and co-workers,[15] in certain organic solvents, for example acetonitrile, the formation of $[I_9]^-$ anions is impossible, because of their complete electrolytic dissociation.

In the $(NMe_4)I-I_2$ [34] and $[Ni(NH_3)_6]I_2-I_2$ [80] systems, the formation of phases with the compositions $(NMe_4)[I_9]$ and $[Ni(NH_3)_6][I_9]_2$ has been established. The conclusion[28,81] that the phase $Rb[I_9]$ may be formed in the $RbI-I_2$ system appears doubtful.[82,83] A large number of syntheses of tetra-alkylammonium nona-iodates has been carried out.[10,11,14,54,84] The data given in Refs.54 and 84 on the compositions of the complexes appear doubtful, however, because of the unsatisfactory methods of chemical analysis.

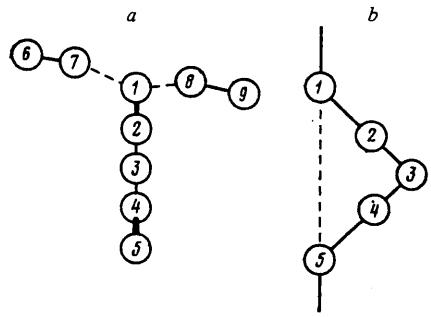



Figure 11. Structure of the $[I_9]^-$ anion in the complex $(NMe_4)[I_9]$;[85] *a*) view from above; *b*) view from the side; interatomic distances (Å): 1–2 = 3.18; 2–3 = 2.90; 3–4 = 3.24; 4–5 = 2.91; 6–7 = 2.67; 8–9 = 2.67; 7–1 = 3.43; 8–1 = 3.24; angle 2–3–4 = 86.5°.

Up to the present, only the structure of $(NMe_4)[I_9]$ (Fig.11) has been studied in detail.[85] The anion contains as complex-forming species the $[I_3]^-$ ion, which coordinates three iodine molecules, two of which lie in the same plane and have interatomic distances which are almost the same as in crystalline iodine. The third iodine molecule is strongly polarised. The unusual arrangement of the ligands is also apparently responsible for the asymmetry and bending of the complex-forming species. This anion can be provisionally regarded as the tris(di-iodine)tri-iodate anion $[(I_3)(I_2)_3]^-$. The thermodynamic characteristics of the reaction

$$(NMe_4)[I_5]\text{(crystalline)} + 2I_2\text{(crystalline)} = (NMe_4)[I_9]\text{(crystalline)}$$

are $\Delta G^0_{298} = -8.9 \pm 0.4$ kJ mole$^{-1}$, $\Delta H^0_{298} = -1.3 \pm 0.8$ kJ mole$^{-1}$, and $\Delta S^0_{298} = 25.9 \pm 2.5$ J mole$^{-1}$ K$^{-1}$.[41]

The reported existence of the polyiodo-iodate $(NMe_4)[I_{10}]$ [33] in the $(NMe_4)I-I_2-C_6H_5Me$ system at 6 °C appears doubtful.

## VI. UNDECA-IODIDES

The possible formation of a polyiodo-iodate containing the $[I_{11}]^-$ anion has been demonstrated in only one paper,[33] describing a study of the $(NMe_4)I-I_2-C_6H_5Me$ system at 6–25 °C. According to these data,[33] a phase with the composition $(NMe_4)[I_{11}]$ crystallises over a fairly wide iodine concentration range: 2.27–9.41 mass % at 6 °C, and 3.53–14.7 mass % at 25 °C. In aqueous ethanol (95%) solutions, tetramethylammonium undeca-iodide is stable only in an extremely narrow iodine concentration range.

The structure of the $[I_{11}]^-$ anion has not been determined, but it may be assumed that it is similar to that of the $[I_9]^-$ anion, except that the inner sphere contains four iodine molecules, two on each end of the $[I_3]^-$ ion.

A study of the $[Ln(ur)_5]I_3-I_2-H_2O$ † systems (0 °C and 25 °C), where Ln represents various lanthanides, detected [85–88] the formation of only one new phase, with the composition $[Ln(ur)_5]I_3.4I_2.10H_2O$, which separated as large acicular hexagonal crystals, incongruently soluble in water. The suggestion that this compound contains the $[I_{11}]^-$ anion has not been confirmed. The new phase apparently contains either the $[I_5]^-$ ion ($[Ln(ur)_5I][I_5]_2.10H_2O$) or chain anions built into the cation matrix.

Anions with the composition $[I_{13}]^-$ have not been detected in any of the polyiodo-iodates synthesised. The preparation of substances with anions containing more than 13 iodine atoms is even less likely. The reaction of iodine with ferrocene in acetone or chloroform gives a black powder with the composition $[Fe(C_5H_5)_2].10I_2$, which decomposes when heated to 170 °C to give iodine and ferrocene, [19] but the actual nature of this substance is still not known.

Thus discrete polyiodo-iodate anions contain not more than 5–7 iodine atoms. The $[I_9]^-$ and $[I_{11}]^-$ anions are rather oligomeric chain anions. If conditions are created for a further increase in the number of iodine atoms in the anion, the latter becomes polymeric, and consists chiefly of $[I_3]^-$ and $[I_5]^-$ ions.

## VII. POLYIODO-IODATES WITH CHAIN ANIONS

The tendency for iodine molecules to form chain polyiodo-iodate anions $[I_x]^-_\infty$ ($x$ = 3, 5, or 7) is often observed when the molecules of substances reacting with iodine have a planar configuration and are able, after oxidation, to form a "stacked" structure containing cavities and channels with dimensions and geometry comparable with those of the polyiodo-iodate chain. [89]

When the chains are not commensurate with the framework of the substance, the latter contains solvent molecules in its channels, as established [90] for the crystals of [(TMA).0.09H][$I_5$].0.7$H_2O$.# The polyiodo-iodate chains in this complex consist of $[I_5]^-$ ions (Fig.12), and do not have a fixed position. In other polyiodo-iodates, some of the channels are occupied by iodine chains, and some by solvent molecules, for example $[Pd(bqd)_2][I_x].0.5C_6H_4Cl_2$.§ [91]

In various organic and inorganic polymers containing cavities of appropriate size, the cavities can be occupied by quasi-one-dimensional chains of iodine atoms.

A polyiodo-iodate chain generally consists of $[I_3]^-$ or $[I_5]^-$ ions or their various combinations. Less frequently, the chains contain $[I_7]^-$ ions. If the chains containing $[I_3]^-$ ions are represented as ...I(1)–I(2)–I(3)...I(1)–I(2)–I(3)..., it may be assumed that the distance I(1)–I(2) and I(2)–I(3) vary in the range $R - \delta$, and the distances I(3)...I(1) in the range $R + 2\delta$, where $R$ = 2.95–3.28 Å, and $\delta$ = 0.15–0.35 Å. The most stable structure is that with linear chains, in which $R$ = 3.2 Å and $\delta$ = 0.15 Å. [92] For linear chains containing $[I_5]^-$ ions, ...I(1)–I(2)–I(3)–I(4)–I(5).....I(1)–I(2)–....., the interatomic distances I(1)–I(2) are $R - \varepsilon$, and the distances I(2)–I(3) and I(3)–I(4) are $R + \delta$, and the most stable structure is that with $\varepsilon$ = 0.5 Å. [92]

The channels of the stacked structures are not always completely filled by the chain anions. For example, in (TTF)[$I_x$]¶ they occupy only 40–50% of the volume, [93] so that the chain anions have little influence on one another.

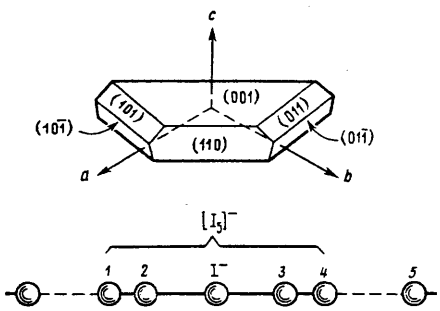



Figure 12. Crystal habit of [(TMA).0.09H][$I_5$].0.7$H_2O$ and a fragment of a polyiodo-iodate chain; [90] interatomic distances (Å): 1–2 = 2.74; 2–I$^-$ = 3.26; I$^-$–3 = 3.26; 3–4 = 2.74; 4–5 = 3.50; 1–5 = 15.5.

Ordered regions ($[I_3]^-$ and $[I_5]^-$ ions) and disordered regions (the intermediate regions between the chains) alternate in the quasi-one-dimensional polyiodo-iodate chains. The disordered regions can be regarded as amorphous one-dimensional formations. [51,94–97]

Phase transformation to a completely ordered structure throughout the chain is not observed above 20 K. [95,98]

Three types of polyiodo-iodate with polymeric anions are examined below: polyiodo-iodates of heterocyclic compounds (mainly aromatic), coordination compounds of *d* elements with macrocyclic ligands, and polymeric carbohydrates.

### 1. Polyiodo-iodates of Heterocyclic Compounds

Many heterocyclic compounds react with iodine or its mixtures with KI in inorganic solvents or aqueous solutions: tetrathiofulvalene, tetrathiotetracene, tetraselenotetracene, tetracyanoquinodimethane, thiopyranylidene, phenazine, thiophenazine, etc. The reaction products are isolated by isohydric or isothermal crystallisation as acicular crystals containing polyiodo-iodate chains.

In the compound $(TTT)_2[I_3]_{1+x}$ † ($x$ = 0.012–0.1), [99–114] the stacked cations with an interplanar distance of 3.32 Å [103,109,110] contain channels occupied by linear chains of symmetric $[I_3]^-$ ions joined to one another; the interionic distance is 3.00–3.64 Å (Fig.13). The non-stiochiometry of the compound is due to the appearance of iodine molecules in the chain. The greatest non-stoichiometry of the polyiodo-iodate chain is observed when $(TTT)_2[I_3]_{1+x}$ is recrystallised from a solution, heated to 95 °C, in nitrobenzene containing $3 \times 10^{-3}$ M TTT at a molar ratio iodine/TTT = 1 and a cooling rate of 3 K $h^{-1}$. [101] Crystals with the stoichio-

† ur = urea.

# TMA = trimesic acid, $C_6H_3(COOH)_3$.

§ bqd = o-benzoquinone dioximate.

¶ TTF = tetrathiofulvalene.

† TTT = tetrathiotetracene.

metric composition can be obtained by decreasing the TTT concentration, the molar ratio iodine/TTT, and the cooling rate.

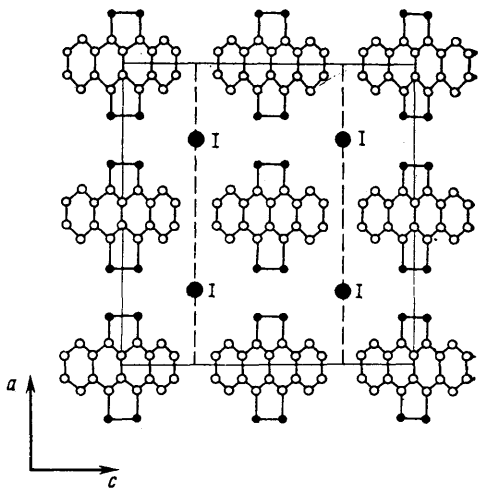



**Figure 13.** [010] projection of the compound $(TTT)_2[I_3]$;[102, 110] the small black and open circles represent the atoms of sulphur and carbon respectively; the polyiodo-iodate chains lie at right angles to the plane of the Figure and are denoted by large black circles.

To obtain single crystals of $(TTT)_2[I_3]$, it is recommended[114] that the substance be crystallised from a gaseous mixture of TTT and iodine, passed in separate streams into a special crystallisation vessel.

In another method, aqueous solutions of TTT acetate and potassium or sodium iodide are mixed.[113]

When the sulphur atoms in the TTT molecule are replaced by selenium atoms (tetraselenotetracene, TSeT), the structure of the polyiodo-iodate chain is altered; in addition to $[I_3]^-$ ions, it also contains $[I_5]^-$ ions.[108,115–119] Three homogeneity ranges have been detected for the compound $(TSeT)_2[I_3]_x$ ($x = 0.17–0.40$):[118] a phase (A) ($x = 0.17$), a phase (B) ($x = 0.24$), and a phase (C) ($x = 0.26$). It is considered[118] that only the phases (B) and (C) contain $[I_3]^-$ and $[I_5]^-$ ions in the chains. Complete charge transfer to the polymeric anion has been established for the phase (A), which is also the phase with the highest electrical conductivity.

The reaction of iodine with tetrathiofulvalene (TTF) in benzene or acetonitrile gives four new phases, depending on the original component ratio: two stoichiometric, $(TTF)_3.[I_3]_2$ and $(TTF)[I_3]$, and two non-stoichiometric, $(TTF).[I_3]_x$ ($x = 0.24–0.26$) and $(TTF)[I_3]_x$ ($x = 0.77–0.87$).[120–128] The syntheses almost always give a mixture of these phases, which are difficult to separate. In the solid-phase synthesis, the number of new phases formed decreases to two: $(TTF)[I_3]$ and $(TTF)[I_3]_x$ ($x = 0.23$).[129]

In all TTF polyiodo-iodates, the stacked structure of the cation contains zigzag chains consisting of $[I_3]^-$, $[I_5]^-$, and $I^-$ ions and iodine molecules.[120,122,124,126] This non-uniform composition of the chains is apparently due to the presence in the new phases of an appreciable number of different trace components and to the difficulty of separating the reaction products.

For the reaction

$$(TTF)(\text{crystalline}) + 3/2\ I_2(\text{crystalline}) = (TTF)[I_3]\,(\text{crystalline})$$

the quantities $\Delta G^0_{298}$, $\Delta H^0_{298}$, and $\Delta S^0_{298}$ are $-5.4 \pm 0.4$ kJ mole$^{-1}$, $-15.1 \pm 0.8$ kJ mole$^{-1}$, and $32 \pm 1.3$ J mole$^{-1}$ K$^{-1}$ respectively.[130]

Tetraselenofulvalene polyiodo-iodates $(TSeF)[I_3]_x$ have been synthesised, but the chain structure of the anions has not yet been studied in detail.[131]

Quasi-one-dimensional polyiodo-iodate chains have been detected in (TPDTP)[$I_x$]# ($x = 2.2–3.4$).[132,133] The polymeric anions consist of either $[I_3]^-$ ions ($x = 2.2$) or a combination of $[I_3]^-$ and $[I_5]^-$ ions ($x = 3.4$). The interionic distances in the $[I_3]^-...[I_3]^-$ chains are 5.49 Å.[132] in the reaction with iodine, the TPDTP molecule loses 0.76–0.90e.

Phenazine (P), phenothiazine (PT), and their derivatives can be oxidised by iodine either in solution in benzene or ether or by thoroughly grinding the starting materials in small quantities of these solvents.[94,95,133–136] The oxidation products have the composition P[$I_x$] ($x = 1.5–1.6$) and $(PT)[I_3]$, and have polyiodo-iodate chains containing asymmetric $[I_3]^-$ ions and $[I_5]^-$ ions.[134,136] The distance between the $[I_3]^-$ ions in the chain is 3.7–3.9 Å.[95]

Quasi-one-dimensional chains consisting of $[I_3]^-$ anions, with an interionic distance of 3.68 Å,[133] have been detected in the crystal structure of $(NMe_4)^+(TCNQ)^{-2/3}[I_3]^-_{1/3}$ § and its derivatives.[137–141] When the tetramethylammonium cation is replaced by the isopentyldimethylammonium cation, the chains acquire quasi-three-dimensional character.[133] The phase transformation of $(NMe_3H)(TCNQ)[I_3]$ at 150 K does not influence the structure of the polyiodo-iodate chains, and alters only the order in which they are arranged.[141]

All the above polyiodo-iodates have cations with a stacked structure, and belong to the group of radical-cation salts.

### 2. Polyiodo-iodates of Polymeric Carbohydrates and Hydrocarbons

Macromolecular carbohydrates (amylose, cyclodextrins, polyvinyl alcohol) and hydrocarbon (polyacetylene, etc.) react in aqueous solution with iodine or its mixtures with KI to form strongly coloured products containing chains of $[I_3]^-$, $[I_5]^-$, and $[I_7]^-$ ions in the channels and cavities of their matrices.

In the channels of amylose (Am), the chains consist chiefly of $[I_5]^-$ ions.[49,142–155] When the solid complexes $Am[I_5]_\infty$ are heated slightly, partial decomposition of the anions to $[I_3]^-$ and iodine takes place.[150] The interionic distance in the chain (3.1–3.5 Å) indicates appreciable interaction of the anions along the chain. The complex with the composition $Am[I_5]_\infty$ contains 50–500 iodine atoms, if there are 3.9 glucose units for every iodine atom.[148,151] Depending on the degree of polymerisation of amylose (the length of its spirals), the concentrations of iodine and iodide ions in the chain may include other ions: $[I_7]^-$, $[I_8]^{2-}$, and $[I_6]^{2-}$. With increase in the length of the chains,

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# TPDTP = tetraphenyldithiopyranylidene.

§ TCNQ = 7,7,7,6-tetracyanoquinodimethane.

the maximum of the absorption band in the electronic spectra at 580 nm is displaced to 630 nm with a simultaneous increase in the molar absorptivity.[146]

The average decrease in enthalpy in the formation of $Am[I_5]_\infty$, calculated for one glucose structural unit and one mole of combined iodine, is −5.2 kJ mole$^{-1}$.[149]

The polyiodo-iodates of cyclodextrins (CD) have different compositions, depending on the synthesis conditions: $(\alpha\text{-CD})_2M[I_5].8H_2O$ (M = Li, Na, Tl), $(\alpha\text{-CD})_2M[I_5].27H_2O$ (M = K, $NH_4$, Ca, Sr, Zn, Cd), $(\alpha\text{-CD})_2M[I_5].(12–19)H_2O$ (M = K, $NH_4$, Rb, Cs).[149,143,150,156–158] The units of the almost linear polyiodo-iodate chain are $[I_5]^-$ ions.

The central $I^-$ atom of each ion of this type is situated between the dimeric molecules of (α-CD) and does not occupy a definite structural position; the amplitude of its movement is about 1.7 Å.[155,156,159]

The metal cations and water molecules are situated outside the channels of the (α-CD) structure, and are separated from the $[I_5]^-$ anions by a distance of about 6 Å, so that their influence on the polyiodo-iodate anion is slight.[45,143]

In the (β-CD)–iodine complexes, the channels of diameter 6.2 Å are occupied by zigzag chains of $[I_7]^-$ ions.[156]

When iodine is added to polyacetylene during its formation in n-hexane, black polymers with the composition *cis*-$(CHI_{0.06})_\infty$ and *trans*-$(CHI_{0.22})_\infty$ separate. The *trans*-isomer was isolated by heating the mixture of polymers in a vacuum or in argon at 180 °C.[160,161] Polyacetylene film is iodinated by treating it with iodine vapour[161] or by immersing it in $CCl_4$ saturated with iodine.[162,163]

Polyacetylene polyiodo-iodates with other compositions, for example $(CHI_x)_\infty$, where $x$ = 0.12–0.23, can also be obtained.[164–168]

According to Ref.168, the surface layer of the polymer fibres contains $[I_7]^-_\infty$ ions. In a vacuum, these ions decompose, leaving only $[I_5]^-$ ions in the chains, and the composition of the polymer approaches $(CHI_{0.15})_\infty$.

Thus each $[I_5]^-$ ion of the linear chain accepts one electron per 33 carbon atoms of the polyacetylene. Other charge-transfer ratios are also observed.

The polyiodo-iodate chains are arranged between the fibres of the polymer[169] in different ways.[168–171]

The chains of *cis*-$(CHI_{0.23})_\infty$ contain 93% $[I_5]^-$ ions and 7% $[I_3]^-$ ions;[162] the $[I_5]^-$ ion is linear, with a symmetrical charge distribution. When the substance is kept for a long time in a vacuum, the concentration of $[I_3]^-$ ions in the chain increases. An interesting feature is that the ratio of $[I_3]^-$ and $[I_5]^-$ ions in the chains alters when the polyacetylene films are stretched.[98] According to Ref.163, the ions predominating in the polymer $(CHI_x)_\infty$ are $[I_3]^-$ and $[I_5]^-$ at $x \leq 0.1$, $[I_5]^-$ at $x \geq 0.12$, and $[I_7]^-$ at $x > 0.3$.

In the spiral structure of polyvinyl alcohol, the polyiodo-iodate chains consist of $[I_3]^-$ ions.[172–175]

The iodination of polycyclic aromatic compounds (perylene, pyrene, flavone, etc.) gives chain polyiodo-iodates.[176,177] The nature of the chain anions in this case has not been finally established, although the presence of $[I_7]^-$ ions has been assumed.[178,179]

### 3. Polyiodo-iodates of *d* Elements with Macrocyclic Ligands

Polyiodo-iodate chains may be formed in a large number of complex compounds of *d* elements with chelating macrocyclic ligands with a planar configuration (phthalocyanines, tetrabenzoporphyrinates, diphenylglyoximates, benzoquinone dioximates, ethylenediamine complexes of metals, etc.) when these compounds are oxidised by iodine.

Polyiodo-iodate chains are formed in the stacked structure of the cations only when the complex-forming metals are arranged above one another at a relatively short distance of 3.15–3.40 Å.[180] The influence of the iodine atoms on the production of the channels in the stacked structure of the cations has not been proved.

In most cases these polyiodo-iodates are charge-transfer complexes.

The following six groups of complex have been studied in detail: I) diphenylglyoximates with the composition $[M(Hdpg)_2][I_x]$,¶ where $x$ = 0.58–0.68, and M = Ni and Pd;[51,91,181–184] II) benzoquinone dioximates with the composition $[M(Hbqd)_2][I_x]$, where $x$ = 0.5–0.7, and M = Ni and Pd;[91,96,185–188] III) phthalocyanines with the composition $[M(pc)_n][I_x]_n$,† where $x \geq 3$, and M = Cu, Zn, Al, Ga, Si, Cr, Fe, Co, Ni, Pt;[188–195] IV) ethylenediamine complexes with the composition $[M(en)_2][I_3]_2$, where M = Zn, Cd, Ni, Co, Pd;[23,67,89,196–198] V) tetrabenzoporphyrinates with the composition $[Ni(tbp)_2]_2.[Ni(tbp)]^+[I_3]^-$; #[199–201] VI) tetra-azoazulenes with the composition $[M(taa)][I_x]$,§ where $x$ = 0.8–1.9, and M = Cu, Co, Ni, Pd.[202–204]

Polyiodo-iodates with macrocyclic ligands are usually prepared by the same method: the metal chelate and iodine are dissolved in an organic solvent (toluene, dichlorobenzene) with heating, sometimes in the presence of small quantities of KI, followed by slow isohydric crystallisation.[91,185,190,205]

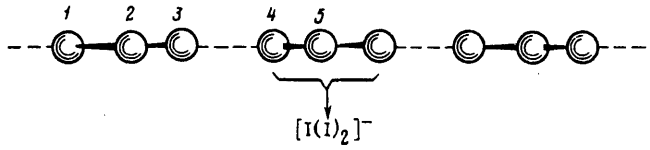



Figure 14. Structure of the polyiodo-iodate anion in $[Ni(Hbqd)_2][I_{0.5-0.7}]$; interatomic distances (Å): 1–2 = 2.96; 2–3 = 2.90; 3–4 = 3.80; 4–5 = 2.90.[96,186]

$[I_5]^-$ anions predominate in the polyiodo-iodate chains of the complexes of the first group, and $[I_3]^-$ ions in the complexes of the second group (Fig.14). Group III also includes the polyiodo-iodates of phthalocyanines with partly oxidised metal-containing macro-rings with the composition $[M(pc)O][I_x]$, where $x$ = 0.5–5.5, and M = Sn, Ge, and Si.[206,207] These substances are stable in air, and lose iodine only when heated above 100°. The anions of the phthalocyanines contain symmetrical $[I_3]^-$ ions with an interionic distance of 3.72 Å.

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¶ dpg = 1,2-diphenylglyoximate.

† pc = phthalocyanine.

# tbp = tetrabenzoporphyrinate.

§ taa = tetra-azoazulene.

The energy characteristics of the formation of phthalocyanine polyiodo-iodates in the reaction

$$[M(pc)]\,(crystalline) + 1/2\,I_2(crystalline) = [M(pc)]\,[I]\,(crystalline)$$

are, for M = Cu, Co, and Ni, $\Delta H^0_{298} = -13.0$, $-16.7$, and $-18.8$ kJ mole$^{-1}$ respectively, and $\Delta S^0_{298} = -24.3$, $-15.5$, and $-33.9$ J mole$^{-1}$ K$^{-1}$ respectively.[130]

Thus the thermodynamic stability of the phthalocyanine polyiodoiodates decreases with increase in the atomic number of the complex-forming element.

In polyiodo-iodates containing ligands with large rings (pc, tbp, tmp,¶ etc.), the chain anion consists of $[I_3]^-$ ions; when the ligands contain small rings, however, the chains contain $[I_5]^-$ ions, for example in the compounds of Ni and Cu with oep.†[208]

Partial oxidation of the metal-containing macro-rings does not alter the nature of the polyiodo-iodate chains. $[I_5]^-$ ions appear in the chains only at a high iodine concentration.[206,207]

In the complexes of groups IV and V, the chains contain asymmetric $[I_3]^-$ ions with an interionic distance of 3.598 Å.[89] Analysis of the Raman and Mössbauer spectra showed that the chains in the compounds of these groups do not contain iodine molecules or $[I_5]^-$ ions.[181,187,199,200]

In recent years, another class of chain polyiodo-iodates has appeared, namely inorganic polymers. Treatment of the polymer $(SN)_\infty$ with iodine vapour (20 mmHg, 350 °C) gives $(SNI_{0.14})_\infty$. In this product, the polyiodo-iodate chains consist of $[I_3]^-$ and $[I_5]^-$ ions, and also strongly polarised iodine molecules.[209,210]

## VIII. SUMMARY

The above data show that the size, configuration, and composition of the polyiodo-iodate anion are determined not only by the cation environment but also by the synthesis conditions.

Sodium, potassium, and rubidium polyiodo-iodates containing more than five iodine atoms are extremely unstable, and it has not yet been possible to isolate them from aqueous solutions as individual solid phases, although a complex with the composition $(NH_4)[I_5]$ has been obtained. This branch of the chemistry of the alkali metal polyiodo-iodates requires further study.

In $(NR_4)I-I_2-H_2O$–organic solvent systems, polyiodo-iodates with all anions from $[I_5]^-$ to $[I_{11}]^-$ may be formed, but there is no system containing tetra-alkylammonium iodides in which a range of crystallisation of octa-iodides has been detected, or in which the crystallisation ranges of all other polyiodo-iodates coexist.

Non-aqueous solvents often stabilise polyiodo-iodate anions and convert the adducts into ionic compounds, but nevertheless, in the $RbI-I_2-C_6H_6$ system, only the tri-iodide, hepta-iodide, and nona-iodide crystallise, but there is no penta-iodide crystallisation range (see Fig.4). If rubidium iodide in this system is replaced by caesium iodide, the hepta-iodide crystallisation range disappears, but a penta-iodide crystallisation range does not appear.

The fact that the number of iodine atoms in the anions of most polyiodo-iodates is odd is noteworthy. This anion composition is determined by the fact that the complex-forming species is always either an iodine atom with positive, negative, or zero charge, or the tri-iodide ion $[I_3]^-$, and the ligands are iodine molecules or iodide ions. In the $[I_8]^{2-}$ anion, the complex-forming species is an iodine molecule. The coordination number in the polyiodo-iodates is 2. The appearance of coordination numbers of 3 in the $[I_9]^-$ ion and 4 in the $[I_{11}]^-$ ion is unusual, and the distorted chain structure of these anions does not agree with the usual ideas about the conformation of ions with analogous coordination numbers. Nona-iodides and undeca-iodides are rather oligomers.

The influence of the crystal field on the geometry, bond order, and charge distribution in the anions is slight. The stability of the anions is greater when the crystal lattice contains large cations. In an asymmetric crystal field, with a rigid non-deformable cation environment, the anions become angular and asymmetric. For example, the $[I_5]^-$ anion is linear only in a vacuum and in the polyacetylene–iodine system, and in other cases it is V-shaped.

The polyiodo-iodate anions being considered are apparently stereochemically non-rigid structures. The determination of their conformation requires allowance for interatomic vibrations which may bring about rearrangement of the nuclei in the chain. The concepts of "equilibrium structure" and "point symmetry of the nuclear configuration" are therefore inapplicable to these anions.

Polyiodo-iodate chains are ordered only in one direction, and even in this case there are appreciably extended disordered regions (the regions between the anions), as is typical of liquids or amorphous solids. Thus these chains are sometimes regarded[94,95] as one-dimensional liquids. The ordered range along the chains increases with decrease in temperature, but complete ordering is not achieved even at 10–30 K.[94]

All chain polyiodo-iodates can be divided into three types. In compounds of the first type, the chains are stabilised by the presence of spiral and cyclic organic molecules with a closed configuration (amylose, α-cyclodextrin, etc.). The channels in compounds of this type may contain two chains, with different interionic distances.[211] In polyiodo-iodates of the second type, the chains are situated in the channels of stacked cations with an open atom configuration (TTT, TTF, etc.). The chains are stabilised by the planar aromatic system containing donor molecules with π electrons, α-pyrone rings, etc. In compounds of the third type, in which the structure of the cations somewhat resembles that of the polyiodo-iodates of the second type, the chains are stabilised by the oxidation of different functional parts of the inner sphere, and by the arrangement of the chelates in a "stack", in which the complex-forming species form a quasi-one-dimensional chain with the minimum possible interionic distance.

In any case, the presence of a stacked cation structure does not necessarily mean that chains of iodine atoms can be produced in it.[212–215]

Polyiodo-iodates have recently been attracting considerable attention. They include substances with metallic conductivity, some of which may be promising for the product of new semiconductors and high-temperature superconductors.[121,184,185,216] Polyiodo-iodates are being tested as components of future hydrogen energy systems[217,218] and opto-electronic devices,[158] and for the production of organic polymers with controllable composition-dependent electrical properties.[219] Polyiodo-iodates are used in medicinal and antimicrobial preparations,[220] in analytical chemistry,[221] and in the separation

¶ tmp = 5,10,15,20-tetramethylporphyrinate.

† oep = 2,3,7,8,12,13,17,18-octaethylporphyrinate.

of materials and the preparation of extremely pure substances.[222]

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# Cluster and Polynuclear Heterogeneous Metal Complex Catalysts

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The present state of the problem of catalysis by cluster and polynuclear transition metal complexes attached to the surfaces of mineral and organic polymers is analysed. The principal methods of preparation of heterogenised clusters and the possible ways of transforming them on the surfaces of carriers are examined and the influence of the nuclearity of the clusters on the catalytic activity and selectivity in the conversion of CO is discussed. The prospects for the employment of immobilised clusters in catalysis are considered.
The bibliography includes 166 references.

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## I. INTRODUCTION

Heterogeneous metal complex catlaysis is a new rapidly developing field of catalytic chemistry. In the first review and monographs,[1-3] the likely usefulness of heterogeneous metal complex catalysts (HMC), containing cluster and polynuclear transition metal complexes attached to a carrier, was already pointed out. During the last 7–8 years, methods of synthesis have been developed and the properties of such catalysts have been investigated. It has been suggested that the cluster HMC manifest a high activity and selectivity in many-electron and multistage chemical reactions as a result of the activation of inert molecules on polynuclear active centres. It is therefore not surprising that the main tests for the catalytic activity of clusters have been reactions involving the simultaneous activation of CO and $H_2$. Some results of these studies are discussed in our previous review.[4]

Numerous investigations of the methods of synthesis of cluster HMC with different nuclearities and of the reactions of the clusters on the surfaces of carriers during catalysis have been published recently. A series of interesting results have been obtained in the investigation of the catalytic activities of these systems and of the influence of the nature of the carrier surface on their catalytic properties. This review is devoted to the analysis of these studies.

Since the terminology in the field of chemistry of cluster and polynuclear compounds has not as yet been finally formulated, we shall explain certain terms employed in this review. A transition metal cluster in catalysis is the name given to a group of $n$ metal atoms ($n \geq 2$) bound to one another. Polynuclear transition metal complexes are compounds whose composition includes two or more metal atoms not linked directly to one another. The nuclearity of the cluster is characterised by the number of metal atoms in its skeleton. The nuclearity of a polynuclear complex is determined by the number of metal atoms in its composition. Homonuclear complexes contain the atoms of only one metal, while heteronuclear complexes contain the atoms of several metals. The interaction of transition metal complexes with the surfaces of carriers, carried out in order to synthesise heterogeneous catalysts, is called heterogenisation. This process can include both pure adsorption interaction and chemical reactions on the surface.

## II. HETEROGENISATION OF CLUSTER CARBONYL COMPLEXES ON UNMODIFIED MINERAL CARRIERS

One of the simplest and most widely used methods for the heterogenisation of cluster and polynuclear complexes is adsorption from solution. Hydroxy-groups and acid and basic Lewis centres are distributed on the surfaces of mineral carriers, so that the interaction between the complex and the carrier may be due not only to weak adsorption forces but also to the formation of strong chemical bonds. The chemical interaction of the complex with the surface usually leads to one of three possible consequences: (1) the cluster skeleton and the oxidation state of the constituent transition metal atoms of the cluster remain unchanged; (2) the skeleton of the complex is preserved, but the oxidation state of the metal atoms changes; (3) the cluster skeleton breaks down. In the last case there is a possibility of both the dispersion of the cluster compound with formation of mononuclear centres on the carrier surface and of an increase in the nuclearity of the cluster up to the formation of the metallic phase. Unfortunately the possibility of the occurrence of the processes enumerated above on the carrier surface is by no means taken into account in all the studies devoted to catalysis by heterogenised cluster and polynuclear complexes. Since problems associated with the reactions of complexes on the surface are of key importance for the interpretation of the nature of the activity of heterogeneous cluster catalysts (HCC), studies in which the changes in the complexes on heterogenisation were investigated specially are considered below.

Carbonyl complexes, for example, $Mo(CO)_6$, can interact with the surfaces of mineral carriers in accordance with the following schemes:[5]

$$Mo(CO)_6 + |{-}O^- \rightarrow Mo(CO)_5(O^- {-}|);$$
$$[Mo(CO)_3]_{ads} + 2|{-}OH \rightarrow (|{-}O^-)_2Mo^{2+} + H_2 + 3CO.$$

Thus there is a possibility of the strong chemisorption of metal carbonyls on the carrier surface containing basic groups or acid Lewis centres.[6-8] In the heterogenisation of th iron carbonyls $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ on $Al_2O_3$, analogous reactions were observed.[9] At 150 °C the so-called sub-carbonyl species $[Fe(CO)_2]_{ads}$ are formed on the surface.[9,10]

It has been suggested[11,12] that the carbonyl ligand may be attacked by the surface hydroxy-group in the first stage of the interaction of $Fe(CO)_5$ and $Fe_5(CO)_{12}$ with $Al_2O_3$ and MgO and the ionic hydride $[HFe_3(CO)_{11}]^-$ is formed:

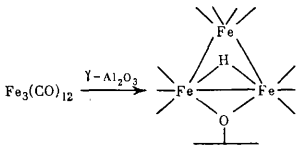
$$Fe_3(CO)_{12} + M-OH- \begin{cases} \longrightarrow (CO_2)_{ads}\ ; \\ \longrightarrow [HFe_3(CO)_{11}]^- M^+\ ; \end{cases}$$

$$3Fe(CO)_5 + M-OH- \begin{cases} \longrightarrow [HFe_3(CO)_{11}]^- M^+\ ; \\ \longrightarrow 3CO + (CO_2)_{ads}\ ; \end{cases}$$

$M=Al^{3+}, Mg^{2+}$.

The rate of reaction of the mononuclear complex with surface hydroxyls is lower than that of the cluster complex. The addition of HCl to the product leads to the regeneration of $Fe_3(CO)_{12}$ according to the authors' data.[11]

On the basis of EXAFS, infrared, and ultraviolet spectroscopic and thermal desorption data, Iwasawa et al.[13] arrived at conclusions differing somewhat from those of Brenner and Hucul[10] and Hugues et al.[11] They showed that a covalently bound $Fe_3$ cluster is formed when $Fe_3(CO)_{12}$ is adsorbed on the surface of $Al_2O_3$ at 40 °C:




$Fe_3(CO)_{12}$ does not interact with an $SiO_2$ surface.[13]

The anionic complex $[Fe_3(CO)_{11}H]^-$ is more stable on an $Al_2O_3$ surface than its covalently bound analogue, which is readily oxidised by atmospheric oxygen even at room temperature.[13] Presumably both structures considered may be formed on $Al_2O_3$ and the predominance of one of them depends on the acid–base properties of the carrier and the concentration of the surface OH groups.

This hypothesis has been to a large extent confirmed by the results of the study of the heterogenisation of $Fe_3(CO)_{12}$ on magnesium oxide dehydrated under mild and severe conditions.[12] The liberation of hydrogen and the appearance of $Fe^{2+}$ are characteristic of a carrier with a high concentration of OH groups on heating to a temperature above 80 °C. At 110 °C the cluster decomposes fully. The complex is fully decarbonylated without evolution of $H_2$ on the surface of MgO dehydrated at a high temperature, and zerovalent iron is oxidised to $Fe^{2+}$. It is assumed[12] that the $[HFe_3.(CO)_{11}]^-$ ions and possibly the compound $Fe(CO)_4(CO_2Mg)$ are formed on the surface with a low concentration of OH groups.

All three iron carbonyls have been heterogenised on the NaY and HY zeolites in order to synthesise catalysts of the Fischer–Tropsch reaction.[14,15] Behaviour analogous to that described above was then observed: when $Fe_3(CO)_{12}$/HY is heated to 60 °C, $H_2Fe_3(CO)_{11}$ is formed on the surface and decomposes on further increase of temperature to 200 °C giving rise to $Fe^{2+}$ ions attached to the zeolite.

The stabilisation of the metal in a low oxidation state has been observed on the NaY zeolite.[16]

The mononuclear carbonyl $Fe(CO)_5$ adsorbed on the HY zeolite is converted into cluster structures on heating:[15]

$$|\text{--OH} + Fe(CO)_5 \xrightarrow{25°C} [Fe(CO)_5]_{ads} + CO +$$

$$+ [|\text{—O}\cdots Fe(CO)_4] \underset{25°C,+CO}{\overset{60°C,-CO}{\rightleftharpoons}} [(|\text{—OH})_3\cdots F_3(CO)_{12}]\ ;$$

$|$—OH= zeolite HY.

Unfortunately specimens obtained to date by the interaction of iron carbonyls with zeolites are inferior as regards the selectivity of the formation of olefins in the Fischer–Tropsch reaction to the analogous HCC based on $Al_2O_3$.

In a study[17] of the heterogenisation of $Ru_3(CO)_{12}$ on $SiO_2$, it was established by the infrared spectroscopic, thermal desorption (25–170 °C), and radiochemical methods that the physical adsorption is followed by the formation of the subcarbonyl species:

$$|\text{—OH} + Ru_3(CO)_{12} \rightarrow (|\text{—O})_xH_yRu_3(CO)_5\ .$$

The resulting catalyst was active in the isomerisation and hydrogenation of olefins at 353–415 K.

On the other hand, Goodwin and Naccache[18] suggest that, although the cluster–carrier interaction, characterised by the appearance of new absorption bands in the infrared spectrum (2134, 2110, and 2119 $cm^{-1}$), is observed in heterogenisation of $Ru_3(CO)_{12}$ on $Al_2O_3$, $SiO_2$, and NaY, the composition and structure of the initial cluster do not change and hydride complexes are formed. The increase in sensitivity of the heterogenised $Ru_3(CO)_{12}$ to oxygen has been explained[18] by the ease of the oxidation reaction

$$Ru_3(CO)_{12} + 6O_2 \rightarrow Ru_3(O)_6(CO)_6 + 6CO_2$$

on the carrier surface.

In a number of instances a distinct tendency towards the formation on the carrier surface of clusters with a rigorously defined nuclearity, regardless of the nuclearity of the initial complex. Thus, when $Rh_4(CO)_{12}$ was attached to the $SiO_2$ and $Al_2O_3$ surfaces at room temperature,[19] a $Rh_6$ cluster was obtained:

$$3Rh_4(CO)_{12} \rightarrow 2Rh_6(CO)_{16} + 4CO\ .$$

The same cluster is formed on the $Al_2O_3$ surface from $Rh_4(CO)_{12}$ and $Rh_2(CO)_4Cl_2$ when the latter are initially decarbonylated and then again brought into contact with CO.[20]

The high stability of $Rh_6$ structures on the carrier surfaces is indicated by the results of a study by Conrad et al.[21] It has been shown by infrared spectroscopy that $SiO_2$ has no influence on the structure of the cluster and that $Rh_6(CO)_{16}$ may be reversibly decarbonylated on the surface of this carrier.

According to spectroscopic data, the interaction of $Rh_6(CO)_{16}/SiO_2$ with water vapour or hydrogen and the adsorption of CO on metallic rhodium lead to the formation of identical structures on the surface:[22]

$$[Rh_6(CO)_{16}]_{ads} \rightarrow \left[\begin{array}{c} CO\ CO\ CO\ CO\ CO \\ |\ \ \ |\ \ \ |\ \ \ |\ \ \ | \\ \text{—Rh—}\ \ Rh\ \ \text{—Rh—} \end{array}\right],$$

When the $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ clusters heterogenised on $Al_2O_3$, $SiO_2$, and MgO are heat-treated, the polynuclear centre decomposes, the $[Rh(CO)_2]$ fragments are formed, and the metal is oxidised:[19,22,23]

$$Rh_6(CO)_{16} + 6X-OH \xrightarrow{100°C} 3\left[\begin{array}{c} (CO)_2\ \ (CO)_2 \\ Rh\ldots\ Rh \\ \diagdown\ \ \diagup \\ O\ \ \ O\ \ \ O \\ |\ \ \ |\ \ \ | \\ X\ \ \ X\ \ \ X \end{array}\right] + 4CO + 3H_2\ ;$$

(A)

X=Al, Mg, Si.

Spectroscopic studies have shown that the metal–metal interaction in the dimer formed is very weak.[19,23]

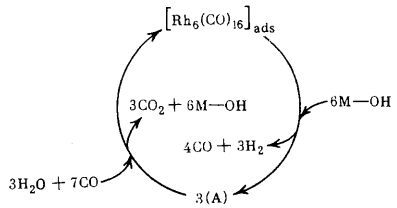
The initial cluster structures can be regenerated by a reductive treatment of the specimens with a mixture of water vapour and CO:[19]

$$2[Rh^I(CO)_2] \rightarrow 2[Rh^0(CO)_n] - \begin{cases} \longrightarrow Rh_x(CO)_y\ ; \\ \longrightarrow Rh_4(CO)_{12} \rightarrow Rh_6(CO)_{16}\ . \end{cases}$$

A highly dispersed metallic phase is formed in the absence of CO.

The regeneration of $Rh_6(CO)_{16}$ on the $Al_2O_3$ surface takes place simultaneously with the regeneration of the hydroxyl coating on the carrier with liberation of $CO_2$.[23]

The extremely high stability of the $Rh_6(CO)_{16}$ cluster makes it possible to set up a closed cycle for the Fischer–Tropsch reaction and the conversion of water vapour:[23]




The same behaviour has been observed for the $Rh_6(CO)_{16}$ cluster heterogenised on the NaY and HY zeolites and for the rhodium clusters immobilised on other mineral carriers.[24] Decarbonylation leads to the fragmentation to rhodium(I) complexes, but the initial structures may be subsequently regenerated.

As already mentioned previously,[12] the character of the interaction of the cluster with the carrier depends significantly on the properties of the surface, which are in many respects determined by the dehydration temperature the infrared spectra of $Rh_4(CO)_{12}$ on lanthanum oxide and $Rh_6(CO)_{16}$ on $\gamma$-$Al_2O_3$ (carriers dehydrated at 600 °C) corresponded to the spectra of the individual clusters.[25–27]

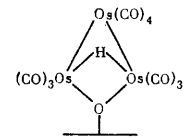
On the other hand, the adsorption of $Rh_6(CO)_{10}$ from solution in chloroform on $Al_2O_3$ dehydrated at a low temperature (200 °C) was accompanied by the partial oxidation of rhodium [the bands of the CO group at 2090 and 2015 $cm^{-1}$, characteristic of $Rh^I(CO)_2$, appeared in the infrared spectrum]. The more reactive $Rh_4(CO)_{12}$ is oxidised even on the carrier dehydrated at 600 °C.

It is essential to bear in mind that the chemical reactivity of the clusters may change on heterogenisation.[20] Thus, $Rh_6(CO)_{16}$, which is stable in air, decomposes partly on the $Al_2O_3$ surface even at room temperature, with evolution of $CO_2$:

$$Rh_6(CO)_{16}/Al_2O_3 + \left(m + n\frac{1}{2}\right)O_2 \rightarrow Rh_6(CO)_{16-n}(O_2)_m/Al_2O_3 + n\,CO_2 \ .$$

On the more inert $SiO_2$ carrier, this type of reaction does not occur.

Much attention has been devoted to the study of the sorption heterogenisation of osmium clusters differing in the nuclearity and nature of the ligands. In the study of the heterogenisation of the osmium clusters $Os_3(CO)_{12}$ and $Os_3(CO)_{10}(MeCN)_2$ on the $SiO_2$ surface at 150° and 25 °C respectively, Besson et al.[28] observed the formation of cluster structures having the composition



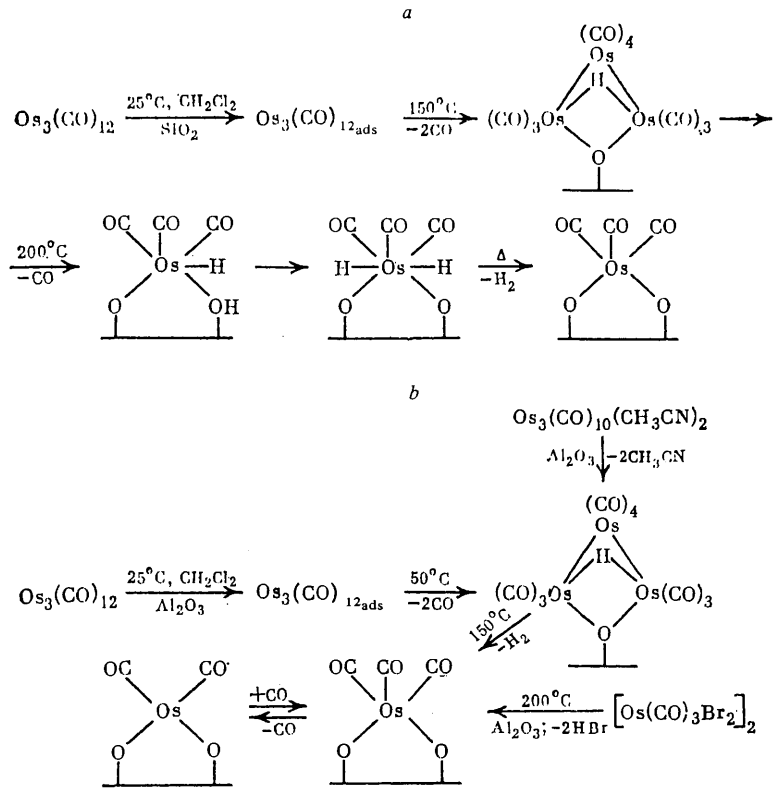
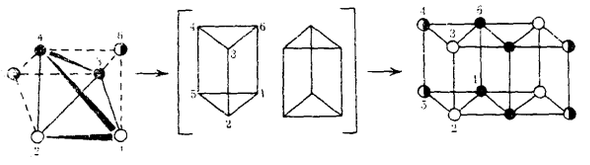




Figure 1. The transformations of the osmium clusters in the course of their heterogenisation on $SiO_2$ and $Al_2O_3$.[29]

The Os–Os distance in the immobilised cluster (2.68 Å) is shorter than in the initial $Os_3(CO)_{12}$ (2.88 Å). Fig. 1 presents the mechanism of the reactions of the osmium clusters heterogenised on $SiO_2$ and $Al_2O_3$ surfaces under the conditions of different types of treatment.[29]

Another rearrangement of the cluster structure has been suggested by Collier et al.,[30] who investigated the heterogenisation of $Os_3(CO)_{12}$ and $Os_6(CO)_{18}$ on the $Al_2O_3$, $SiO_2$, and $TiO_2$ surfaces.[30] When $Os_3(CO)_{12}$ is adsorbed, absorption bands at 442 and 595 nm, characteristic of the $Os_6(CO)_{18}$ cluster, are observed in the diffuse reflection spectra. Three bands in the region of the CO group vibrations have been found in the infrared spectra of the osmium complexes on all three carriers investigated. On the other hand, the spectrum of the initial osmium cluster contains 16 absorption bands in this region. It had been suggested earlier[31] that such simplification of the spectrum is associated with the formation of the mononuclear $Os(CO)_2$ and $Os(CO)_3$ complexes. However, it has been possible to demonstrate[30] that the three absorption bands mentioned above correspond to the vibrations of the CO groups bound to osmium atoms which are partly in negative (1950 $cm^{-1}$), partly positive (2120 $cm^{-1}$), and partly zero (2030 $cm^{-1}$) formal oxidation states. It has been shown for vanadium, chromium, manganese, iron, cobalt, and nickel carbonyls that a ±100 $cm^{-1}$ vibration frequency shift is characteristic of a ±1 change in the oxidation state.[32] Bearing in mind the weakly basic character of the carriers employed, the authors[30] suggested the possibility of the dimerisation of the $Os_6(CO)_{18}$ cluster:



○ – $Os^0$; ◑ – $Os^{+1}$; ● – $Os^{+2}$

The differences between the results of different investigations[29–31] can probably be explained by the fact that their authors used carriers differing in the degree of hydroxylation of the surface and in the reactivity of the hydroxy-groups. In addition, the surface concentrations of osmium were likewise not identical. Unfortunately it is not possible to take into account the effect of these factors quantitatively.

The study of the heterogenisation of clusters on the surfaces of mineral carriers has shown that the strength of the complex–carrier bond depends both on the nature of the transition metal atoms forming part of the composition of the cluster [for example, $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, $Co_4(CO)_{12}$> $Ir_4(CO)_{12}$ > $Rh_6(CO)_{16}$ > $Ru_3(CO)_{12}$] and on the nature of the carrier (the adsorption on $\gamma$-$Al_2O_3$ is much stronger than on $SiO_2$).[33] It is significant that the adsorption of the molecules of cluster metal carbonyls containing bridging CO groups on $Al_2O_3$ is accompanied by the elimination of these groups. Decarbonylation is promoted by the dissolved oxygen. As a result, a stronger complex–carrier bond arises than might have been expected for adsorption heterogenisation via van der Waals forces.

The transformations of the clusters on the carrier surfaces are extremely complex. Thus, according to infrared spectroscopic data, the structure of the cluster does not change on heterogenisation of $Ru_3(CO)_{12}$ on the surface of $\gamma$-$Al_2O_3$.[34] On the other hand, two anionic complexes are formed on MgO:

$$3Ru_3(CO)_{12} + 2MgO \rightarrow [HRu_3(CO)_{11}]^-/MgO + [Ru_6(CO)_{18}]^{2-}/MgO \ .$$

In this case MgO exhibits "alkaline" properties.[35,36]

The dependence of the adsorption of the $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, and $Ru_6C(CO)_{17}$ on the $\gamma$-$Al_2O_3$ dehydration temperature has been investigated by infrared spectroscopy.[7] Under the conditions of weak dehydration (at temperatures below 300 °C), the absorption bands of the CO groups of the adsorbed $Ru_3(CO)_{12}$ undergo a bathochromic shift, which indicates the appearance of a negative charge in the cluster skeleton as a result of the interaction with the hydroxy-groups of the carrier:

$$Ru{-}CO + \begin{matrix}\diagdown\\ -Al-OH\\ \diagup\end{matrix} \rightarrow \begin{matrix}\diagdown\\ -Al^{\delta+}RuH^{\delta-}\\ \diagup\end{matrix} + CO_2 \ .$$

Under the conditions of vigorous dehydration (at temperatures above 500 °C), the fraction of adsorbed molecules of the complex varies in parallel with the concentration of the Lewis acid centres of the carrier, indicating an interaction of the type $M{-}C{\equiv}O \rightarrow Al^{3+}$. Similar surface compounds have been recorded by infrared spectroscopy in the adsorption of mononuclear nickel,[37] molybdenum,[38] and tungsten[39] carbonyls on $Al_2O_3$.

The hydride carbonyl clusters $H_4Ru_4(CO)_{12}$ [7] and $H_2Fe_3(CO)_{11}$ [40] also form surface anionic complexes by interacting with the hydroxy-groups on the $Al_2O_3$ surface. Some of them proved to be unstable, being transformed in accordance with the mechanism examined with the simultaneous oxidation of the metal and the evolution of CO and $H_2$.[23,25] The transformations of the clusters on $Al_2O_3$ examined above are characteristic also of other oxide carriers.[6,41,42]

In the examples presented above, the coordinated carbonyl ligand is attacked by surface OH groups. Clusters containing acid hydrogen atoms may be deprotonated. For example, the interaction of $H_4Ru_4(CO)_{12}$ ($pK_a$ = 11.7) with $Al_2O_3$ and MgO [43] results in the formation of the anionic cluster $[H_3Ru_4(CO)_{12}]^-$. However, the above feature is not general. In particular, the nucleophilic attack described above, leading to the anion $[H_3RuOs_3(CO)_{12}]^-$, is observed on heterogenisation of the mixed cluster $[H_2RuOs_3(CO)_{13}]$ on $Al_2O_3$.[44] It is noteworthy that the cluster skeleton of the complex obtained is not decomposed by the synthesis gas even at 200 °C.

Thus examination of the studies on the heterogenisation of the carbonyl clusters on the surfaces of mineral carriers leads to the conclusion that it is difficult to predict the state of the complex on the carrier. The composition and structure of the form stabilised on the surface depend on many factors, among which the following may be distinguished: (1) the nuclearity of a cluster; (2) its chemical nature: (3) the nature of the ligands in the coordination sphere; (4) the chemical nature of the carrier; (5) the density of the hydroxyl coating; (6) the heterogenisation conditions.

In addition, analysis of published studies has shown that, even when all the factors enumerated are virtually identical, results may be obtained which lead to different conclusions (see, for example, Refs. 29–31 and 45 and 46).

## III. CATALYTIC ACTIVITY OF THE ADSORPTION-HETEROGENISED CLUSTER AND POLYNUCLEAR TRANSITION METAL COMPLEXES

A general characteristic of processes involving the participation of carbon monoxide (the Fischer–Tropsch reaction, hydroformylation, and carbonylation) is their relatively high exothermicity, i.e. the equilibrium in these reactions is strongly displaced towards the formation of products at room temperature. Nevertheless, real processes are carried out at elevated temperatures, since the activity of industrial catalysts is insufficient for reactions under mild conditions.

It is also known that the selectivity of these reactions is small. For this reason, the application of heterogenised transition metal clusters, which have a fairly uniform set of active centres and promote the many-electron activation of CO, has aroused interest. However, one should bear in mind that, under the conditions of catalysis, the heterogenised clusters as a rule undergo further transformations and their structure frequently differs from the initial structure.

Before being introduced into the catalytic reaction, the heterogenised clusters are usually activated thermally or chemically. The heat treatment is carried out both *in vacuo* and in an atmosphere of CO or the synthesis gas. We may note that even the rate of heating can influence significantly the degree of dispersion of the particles formed. Thus it has been established[47–49] that, on rapid heating (50 K $min^{-1}$) of $Co_2(CO)_8$ specimens on $TiO_2$, $Al_2O_3$, $ZrO_2$, and $SiO_2$, "superparamagnetic" cobalt species are formed and are characterised by a narrow signal in the ferromagnetic resonance (FR) spectrum. When the temperature is raised slowly, relatively large particles, giving rise to a broad signal in the spectrum, are produced.

Chemical activation usually reduces to the oxidation-reduction treatment of the heterogenised clusters. It has been noted[8] that preliminary oxidation of the carbonyl clusters or their decomposition in a stream of inert gas leads to the formation of more dispersed metal particles on the surface of the carrier than direct reduction with hydrogen.[50,51]

When heterogeneous catalysts are employed, it is essential to take into account the texture of the carrier. The effect of the carrier structure on the selectivity of the Fischer–Tropsch reaction has been noted.[52] The catalyst obtained as a result of the heterogenisation of $Co_2(CO)_8$ on $Al_2O_3$ and decomposed at 200 °C is active in the conversion of the synthesis gas into a mixture of linear $C_2$–$C_{20}$ paraffins ($CO:H_2 = 1:2$; 200 °C; 0.1 MPa). The average molecular weight of the paraffin fraction then depends on the effective radius of the carrier pores $r$: 80% of $C_3$–$C_{10}$ paraffins is formed on a narrow-pore carrier ($r = 65$ Å), whereas 80% of the $C_{14}$–$C_{21}$ paraffins are formed on the specimen with $r = 3000$ Å). It may be that the difference between the selectivities is caused by the different degrees of dispersion of cobalt on the two carriers.

The possibility of regulating the selectivity of the Fischer–Tropsch process by altering the nuclearity and composition of the cluster and also of the nature of the carrier has been examined.[53–58] An important result of these investigations is the direct preparation of ethanol from the synthesis gas under relatively mild conditions, which leads to the prospect for the synthesis of ethylene from coal via a process with a small number of stages. The dependence of the yield of ethanol (per atom of rhodium) on the nature of the cluster (with $La_2O_3$ as the carrier) can be represented by the series $[Rh_4(CO)_{12}] > [Rh_6(CO)_{16}] > [Rh_7(CO)_{16}](NEt_4)_3 > [Rh_{13}.(CO)_{23}H_{2-3}](NBu_4)_2$. The following rules have been established:[55] mainly ethanol is formed at temperatures above 200 °C, while at lower temperatures the product is methanol; highly basic carriers (ZnO and MgO) promote the formation of methanol, while basic carriers with weak acidity ($CeO_2$, $La_2O_3$, $TiO_2$, $ZrO_2$, and $ThO_2$) promote the formation of ethanol; weakly acid oxides ($\gamma$-$Al_2O_3$, $V_2O_5$, $WO_3$, and $Al_2O_3$–$SiO_2$) lead to the preferential formation of methane and higher hydrocarbons; the heterogenisation of the $Rh_2$–$Rh_6$ clusters leads to an increase of the selectivity of the conversion into ethanol, while in the presence of the $Rh_7$–$Rh_{13}$ clusters mainly methane and the $C_2$–$C_4$ hydrocarbons are formed.

The synthesis of methanol from CO and $H_2$ (mixture with the ratio $CO:H_2 = 1:2$) in the presence of catalysts obtained as a result of the adsorption heterogenisation of the platinum cluster $[Pt_{15}(CO)_{30}](NEt_4)_2$ on Group IIA, IIB, IIIA, and IVA metal oxides has been described.[54] The highest selectivity of the conversion into methanol, reaching 98%, has been observed for the catalyst on MgO.

Naturally, the process selectivity is greatly influenced also by the nature of the metal: the rhodium clusters immobilised on lanthanum and zirconium oxides promote the selective formation of ethanol, whereas only methane was obtained in the presence of platinum and iridium complexes under identical conditions.[53]

$Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, $Ru_6C(CO)_{17}$, and $RuCl_3$ deposited on $\gamma$-$Al_2O_3$ have been used in the Fischer–Tropsch reaction.[59,60] It has been established that, with increase of the degree of dispersion of the metallic particles, the specific catalytic activity falls and the fraction of light hydrocarbons in the product increases. The authors explain this effect by the strong interaction of the metal with the carrier. It is believed[59,60] that only the centres coordinating one CO molecule are active. The surface subcarbonyl $Ru(CO)_2$ species are stable at the reaction temperature in an atmosphere of hydrogen, which is probably the cause of their catalytic inertness.

In the previous Section it was shown that the nature of the carrier can influence strongly the structure of the product of the heterogenisation of the clusters. It is therefore also not surprising that, when the same cluster complex is deposited on different carriers, active centres of different composition and structure are produced. Thus, when $Ru_3(CO)_{12}$ is heterogenised on $\gamma$-$Al_2O_3$, microcrystalline metallic ruthenium exhibits catalytic activity, which is confirmed by the composition of the products of the Fischer–Tropsch reaction.[34] The anionic complex $[Ru_6C(CO)_{16}]^{2-}$ proved to be responsible for catalysis on MgO. The same complexes were obtained also when $H_4Ru_4(CO)_{12}$ was heterogenised on $Al_2O_3$ and MgO. However, an active catalysis could not be synthesised by adsorbing $K_2[Ru_6C(CO)_{16}]$ on $Al_2O_3$. The authors[34] explained this by the fact that the interaction of $[Ru_6C(CO)_{16}]^{2-}$, formed when the neutral complexes $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ are heterogenised on $Al_2O_3$, differs from the interaction of $K_2[Ru_6C(CO)_{16}]$. We may note that the compositions of the products of the Fischer–Tropsch reaction on $Ru_3(CO)_{12}/MgO$ and $Ru_3(CO)_{12}/Al_2O_3$ differ markedly. The experimental results described show that it is difficult to predict the catalytic properties of heterogeneous cluster catalysts.

Together with the cluster complexes of noble metals, catalytic activity in the Fischer–Tropsch reaction is shown also, as already mentioned above, by the cluster and polynuclear complexes of other Group VIII metals immobilised by adsorption on the surfaces of mineral carriers, for example by $Fe_3(CO)_{12}$ on a type HY or NaY zeolite.[56] The activity of this catalysis is relatively low: liquid hydrocarbons are formed only at 250 °C and 2 MPa (the degree of conversion is 85% after 15 h). The catalysts based on the dinuclear cobalt complex $Co_2(CO)_8$ immobilised on mineral carriers of different nature was active in the conversion of the synthesis gas into a mixture of liquid hydrocarbons only after reduction in a stream of hydrogen at 150 °C.[57,58] n-Alkanes are formed preferentially on the least active carrier, while isoparaffins are formed on strongly acid carriers. Although hydrocarbons ranging from $C_5$ to $C_{22}$ were detected in the mixture, the bulk of the latter consisted of $C_9$–$C_{13}$ paraffins. In analysing the results of this study,[57,58] one cannot rule out the possibility of structural isomerisation of hydrocarbons on a strongly acid carrier.

It is noteworthy that metallic catalysis obtained on the basis of heterogenised iron clusters are active in the hydrogenation of olefins.[61]

Linear hydrocarbons are mainly formed in the hydrogenation of CO on cobalt catalysis prepared by the thermal decomposition of $Co_2(CO)_8$,[62,63] the distribution of their molecular weights obeying the Schultz–Flory equation.[64] The catalysts obtained by the rapid decomposition of the deposited metal carbonyl are 2–10 times more active than the traditional cobalt catalysts.

The same rules hold for the heterogenised cobalt catalytic systems[65] as for the ruthenium systems:[59,60] an increase in the degree of dispersion of the metallic particles lowers the specific catalytic activity; with increase of the metallic particle size, the relative yield of higher hydrocarbons rises, the maximum yield being obtained using $TiO_2$ and $ZrO_2$ as the carriers.[63,66] The $Co_2(CO)_8$ clusters deposited on $SiO_2$ and $TiO_2$ showed the maximum activity.[65]

Pyrolysis of $Fe(CO)_5$ and $Fe_3(CO)_{12}$ on the $\gamma$-$Al_2O_3$ surface yielded selective catalysts of the synthesis of light olefins.[67] However, in the course of the reaction the finely dispersed metallic particles increases in size and methane became the main product. By using the salt-like heteroatomic cluster $(NEt_4[[Fe_2Mn(CO)_{12}]$ as the initial complex, it is possible to increase the stability of the action of the catalyst and to reduce the yield of methane.[69] An attempt to synthesise an active and stable catalyst from the cobalt carbonyl and manganese compounds taken separately was unsuccessful.

In conclusion of this Section, we shall consider the catalytic properties of heterogeneous clusters in the hydroformylation and hydrogenation of olefins and in the dehydrocyclisation of alkanes and the hydrogenation of benzene. Ichikawa[70,71] hydroformylated ethylene and propene on $Co_4(CO)_{12}$/ZnO. Although this catalyst showed a lower activity than the rhodium and rhodium-cobalt clusters, the selectivity of the formation of the linear aldehyde proved to be higher.

The study of the dehydrocyclisation and the structural isomerisation of n-hexane on platinum clusters[72–75] showed that the reaction pathway depends on the number of transition metal atoms in the heterogenised complexes (Table 1). The complexes were deposited on $Al_2O_3$ and $SiO_2$ from solution in tetrahydrofuran. Stoichiometric amounts of CO and triethylamine were evolved on heat treatment of the heterogenised complexes *in vacuo*, in helium, or in hydrogen at 150 to 170 °C and platinum clusters, whose particle size did not exceed 1 nm, were immobilised on the carrier surface.

Table 1. The conversion of n-hexane on heterogenised platinum clusters.[75]

| Cluster | $c^{**}$, wt.% | $T$, °C | Reaction products, mole % | | | |
|---|---|---|---|---|---|---|
| | | | 2-methylpentane | 3-methylpentane | methylcyclopentane | cyclohexane + $C_6H_6$ |
| $[Pt_{15}(CO)_{30}][NEt_4]_2/\gamma$-$Al_2O_3$ | 0.69 | 295 | 17.2 | 8.2 | 61.7 | 12.9 |
| $[Pt_{15}(CO)_{30}][NEt_4]_2/\gamma$-$Al_2O_3$ | 0.69 | 320 | 15.6 | 6.4 | 65.7 | 12.3 |
| $[Pt_{15}(CO)_{30}][NEt_4]_2/SiO_2$ | 0.15 | 320 | 21.4 | 12.5 | 58.5 | 7.6 |
| $[Pt_{12}(CO)_{24}][NEt_4]_2/\gamma$-$Al_2O_3$ | 0.54 | 275 | 1.25 | 6.8 | 64.1 | 13.9 |
| $[Pt_9(CO)_{18}][NEt_4]_2/\gamma$-$Al_2O_3$ | 0.26 | 320 | 9.6 | 6.4 | 72.8 | 11.2 |
| $[Pt_9(CO)_{18}][NEt_4]_2/\gamma$-$Al_2O_3$ | 0.50 | 320 | 11.4 | 5.2 | 74.4 | 9.0 |
| $[Pt_6(CO)_{12}][NEt_4]_2/\gamma$-$Al_2O_3$ | 0.18 | 320 | 5.4 | 3.7 | 83.6 | 7.3 |
| $[Pt_6(CO)_{12}][NEt_4]_2/\gamma$-$Al_2O_3$ | 0.25 | 325 | 5.2 | 2.6 | 87.0 | 5.2 |
| $[Pt_3(CO)_3(PPh_3)_4]/\gamma$-$Al_2O_3$ | 0.45 | 325 | 3.7 | 1.7 | 92.6 | 2.0 |

*After the heterogenisation of the complexes, the specimens were heat-treated at 350 °C (the last row—at 250 °C) in a stream of hydrogen for 5 h.
**The content of metallic platinum.

It follows from Table 1 that the last catalyst is characterised by a high selectivity in the dehydrocyclisation reaction. It may be that structural correspondence, as defined by Balandin, is manifested in this case and that the multiplet made up of three platinum atoms is the most suitable for this reaction.

An anlogous dependence of the selectivity of the reaction on the number of platinum atoms in the heterogenised cluster has been observed in antoher study by Ichikawa.[76] It was found that the catalysts based on the $Pt_{15}$ and $Pt_{12}$ clusters are active both in structural isomerisation and in hydrogenolysis of neopentane, while the $Pt_6$ and $Pt_5$ clusters lead mainly to hydrogenolysis products.

The influence of the nuclearity of the clusters on the activity and selectivity has also been demonstrated.[77] The complexes $Cp_2Ni$, $Cp_2Ni_2(CO)_2$, and $Cp_3Ni_3(CO)_2$ deposited on the silica gel surface from solution in THF showed different catalytic activities after heterogenisation on the carrier and heat treatment *in vacuo* or hydrogen at 120 °C. Thus it was found that acetylene was readily converted into benzene at room temperature (degree of conversion 75% after 2 h) on the nickel catalyst obtained from $Cp_2Ni$, whereas the cluster catalyst proved to be inactive. Under the same conditions, acetylene was firmly adsorbed on the latter (1 mole of $C_2H_2$ per mole of $Ni_3$ or $Ni_2$). On the other hand, the ethylene and benzene hydrogenation reactions, dueterium–hydrogen exchange, and hydroformylation of ethylene occurred only on the cluster catalyst.

## IV. HETEROGENISATION OF POLYNUCLEAR π-ALLYL COMPLEXES

The π-allyl complexes of transition metals are significantly less stable than the carbonyl complexes. Despite the difficulties arising from this fact, the heterogenisation of the π-allyl complexes has been quite widely investigated.[2]

This Section presents the results of the latest studies on the heterogenisation of polynuclear π-allyl complexes and the catalysts based on them.

Detailed studies have been made[78–83] of the heterogenisation of mono- and di-nuclear π-allyl complexes of molybdenum and chromium, which are of a similar chemical nature. The authors endeavoured to elucidate the following questions:

(1) is the structure of the dinuclear centre preserved on heterogenisation; (2) are there differences between the activities of the catalysts obtained by the heterogenisation of the mono- and di-nuclear complexes; (3) does the nature of the mineral matrix influence the character of the immobilisation. The authors established that the Mo–Mo distance in the complex $Mo_2(\pi\text{-allyl})_4$, which amounts to 2.183 Å, increases to 3.1–3.2 Å after heterogenisation. The bond between the molybdenum atoms in this structure is preserved, which has been confirmed by the study of the catalysts using the atomic radial distribution method. The average distance between the $Mo_2 \ldots Mo_2$ pairs in $Al_2O_3$ with a surface concentration of hydroxy-groups of 2.6 $nm^{-2}$ is 23 Å.

Figs. 2 and 3 present schemes for the heterogenisation of $Mo_2(\pi\text{-}C_3H_5)_4$ and $Cr_2(\pi\text{-}C_3H_5)_4$ on five carriers with different specific surfaces and different densities of the hydroxy-groups.

Comparison of the structures obtained by the heterogenisation of mononuclear complexes with the structures derived from their dinuclear analogues shows that the dinuclear molybdenum structures are produced with much more difficulty than the mononuclear structures (Fig. 4). Furthermore, whereas the reduction reaction proceeds in accordance with the scheme $Mo^{6+} \rightarrow Mo^{4+} \rightarrow Mo^{2+}$ for the mononuclear centre, in the case of the dinuclear centre it is possible to detect also the 5+ oxidation state. The $Mo^{3+}$ state was not observed in either case.[83] The variation of the stability of the surface dinuclear structures on $SiO_2$ with the surface

concentration of the immobilised complexes has also been noted: with increase of the concentration, the stability of the structures falls.[83]

The catalytic activities of the immobilised di- and mononuclear complexes differ appreciably. Thus in the oxidative dehydrogenation of ethanol the activity of the mononuclear catalyst is proportional to the concentration of the $Mo^{6+}$ centres, while that of the dinuclear catalyst is proportional to the number of $Mo^{6+}$ pairs (Fig.5). This makes it possible to speak of the cooperative effect of the $Mo^{6+}$ pairs in the catalyst obtained as a result of the immobilisation of the dinuclear π-allyl complex of molybdenum; in other words, this result agrees with Balandin's hypothesis that the dehydrogenation reaction proceeds via a doublet mechanism.

The catalytic properties of the mononuclear and dinuclear molybdenym complexes in a low oxidation state ($Mo^{2+}$) in the hydrogenation of butadiene also proved to be different[83] (Fig.6). Thus, in the presence of the catalyst obtained by the heterogenisation of the mononuclear cluster $Mo(\pi\text{-}C_3H_5)_4$, buta-1,3-diene is mainly converted into a mixture of *cis*- and *trans*-but-2-enes, while in the case of the dinuclear complex but-1-ene is formed in 60% yield. The hydrogenating activity of the dinuclear centre at 0 °C is 5 times greater than that of the mononuclear centre and 3280 times greater than the activity of the traditional impregnated catalyst.

By altering the nuclearity of the active centre and the oxidation state of the transition metal atom forming part of the composition of this centre, it is sometimes possible to

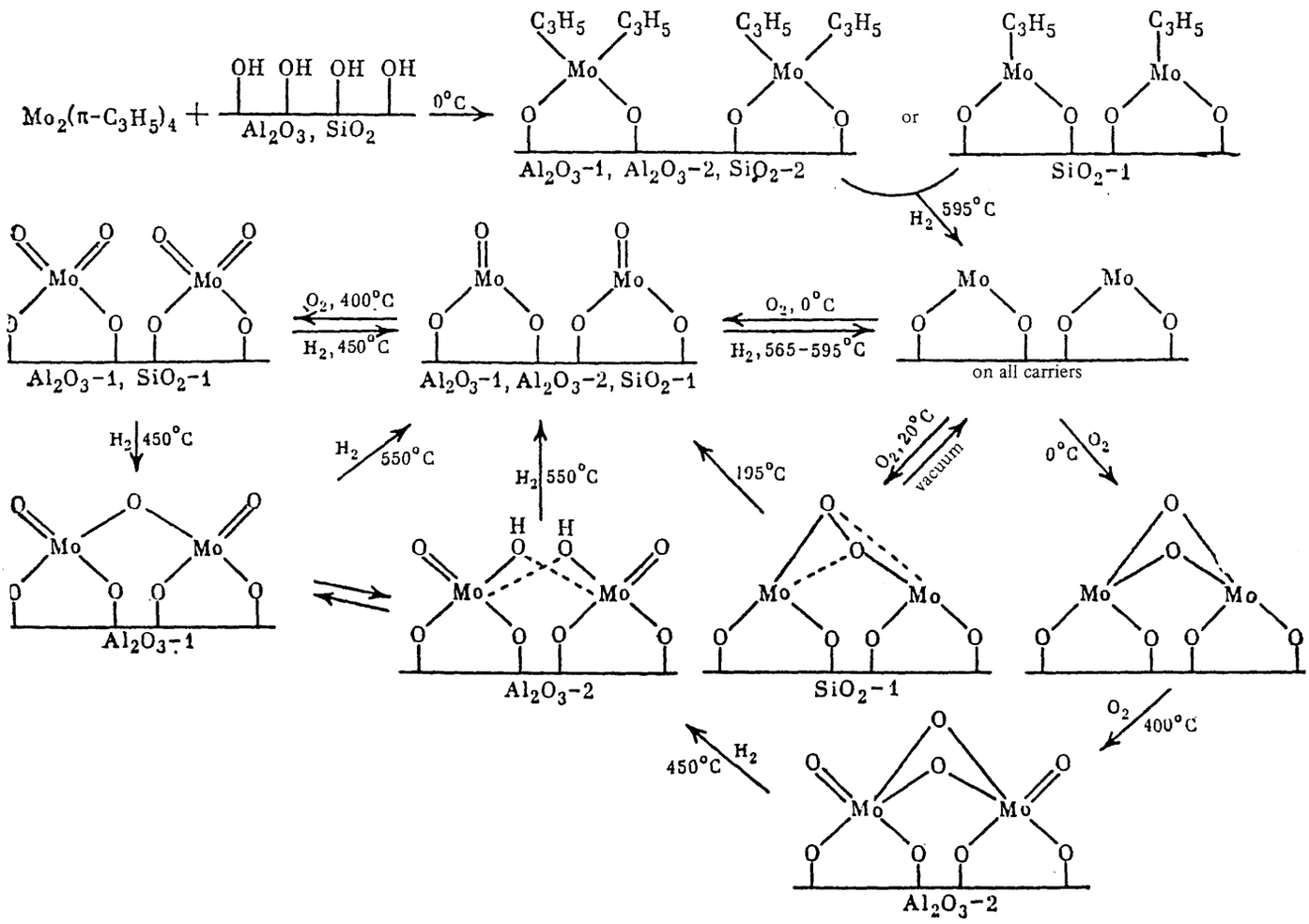
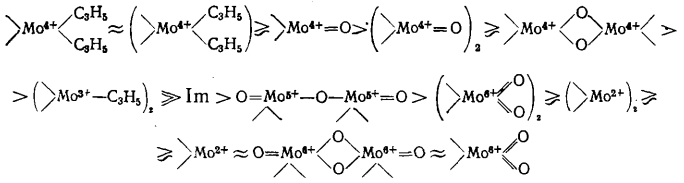
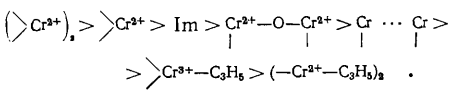



Figure 2. The structures of the surface centres formed as a result of the oxidation-reduction reactions of the dinuclear complex $Mo_2(\pi\text{-}C_3H_5)_4$ heterogenised on carriers of different nature. Carriers: $Al_2O_3$-1 (190 $m^2\ g^{-1}$, 2.6 OH group $nm^{-2}$); $Al_2O_3$-2 (385 $m^2\ g^{-1}$, 4.5 OH group $nm^{-2}$); $SiO_2$-1 (120 $m^2\ g^{-1}$, 3.5 OH group $nm^{-2}$); $SiO_2$-2 (285 $m^2\ g^{-1}$, 4.6 OH group $nm^{-2}$); $SiO_2$-3 (510 $m^2\ g^{-1}$, 1.3 OH group $nm^{-2}$).[78]

discover the structure of the centre which is optimal for the reaction of the given type. This problem has been solved[83] for the disproportionation of propene. The activities of different surface centres, illustrated in Fig.2, diminish in the sequence



where Im is the impregnated catalyst. The activities of the immobilised di- and mono-nuclear π-allyl complexes of chromium in the hydrogenation of propene at −35 °C vary in the analogous sequence:[83]



In this case too the dinuclear centre is more active than the mononuclear centre. This may be explained by the fact that the doublet (as defined by Balandin) is preferable for the hydrogenation reaction.

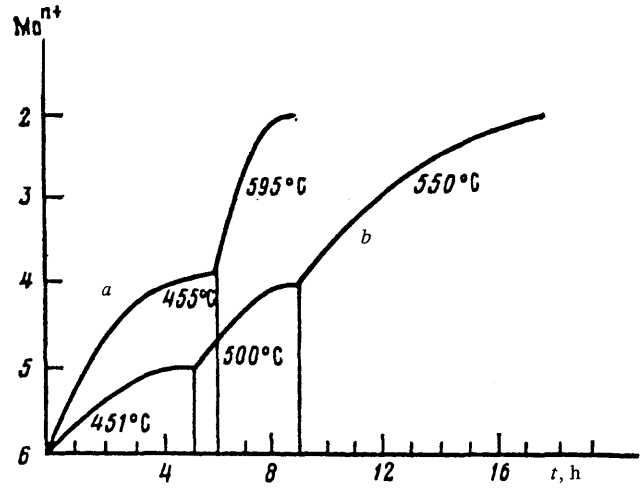



**Figure 4.** Kinetics of the reduction with hydrogen of immobilised mononuclear (*a*) and dinuclear (*b*) π-allyl complexes of molybdenum ($p_{H_2}$ = 64 mmHg).[83]

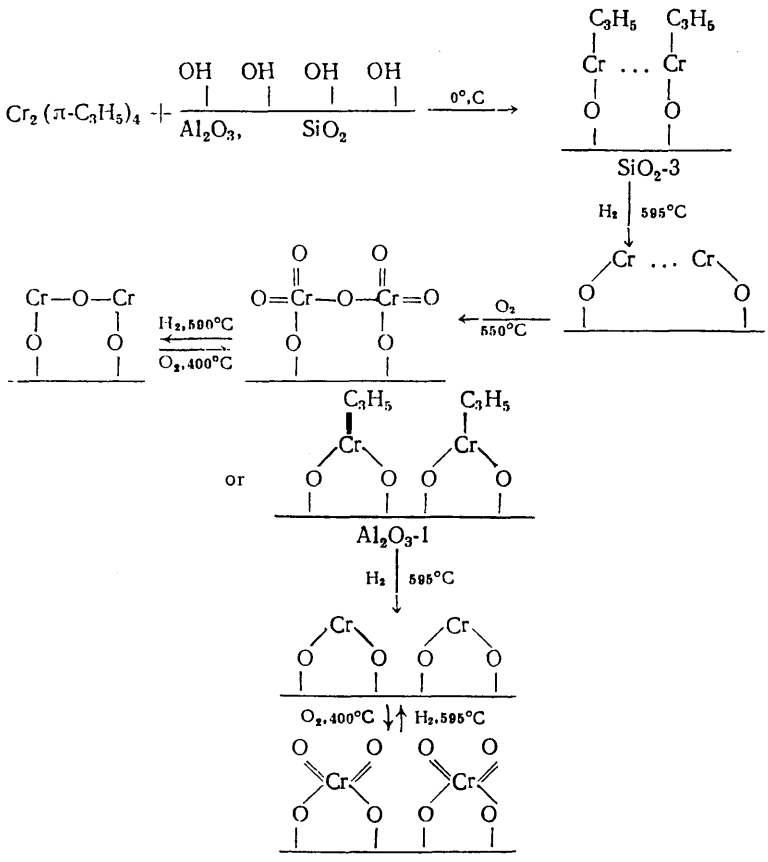



**Figure 3.** The structures of the surface centres formed as a result of the oxidation-reduction reactions of the dinuclear complex $Cr_2(\pi\text{-}C_3H_5)_4$ heterogenised on carriers of different nature; carriers—see the legend to Fig.2.[78]

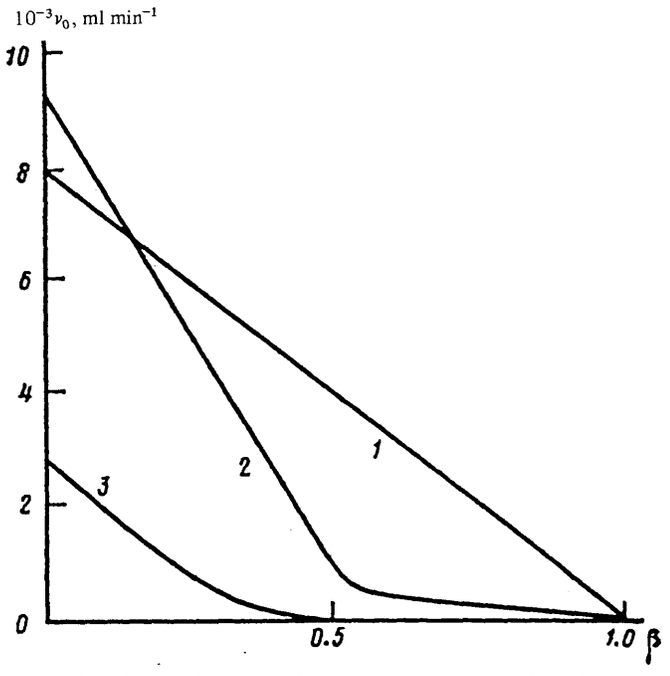



Figure 5. Dependence of the initial rate of the dehydrogenation reaction of ethanol ($v_0$) on the relative content of $Mo^{6+}$ ions ($\beta$) in the oxidised specimens of the immobilised $Mo(\pi\text{-}C_3H_5)_4$ (line *1*) and $Mo_2(\pi\text{-}C_3H_5)_4$ (line *2*) complexes; (*3*) impregnated catalyst based on $(NH_4)_2MoO_4$ ($7.85 \times 10^{18}$ Mo atoms, 148 °C).[83]

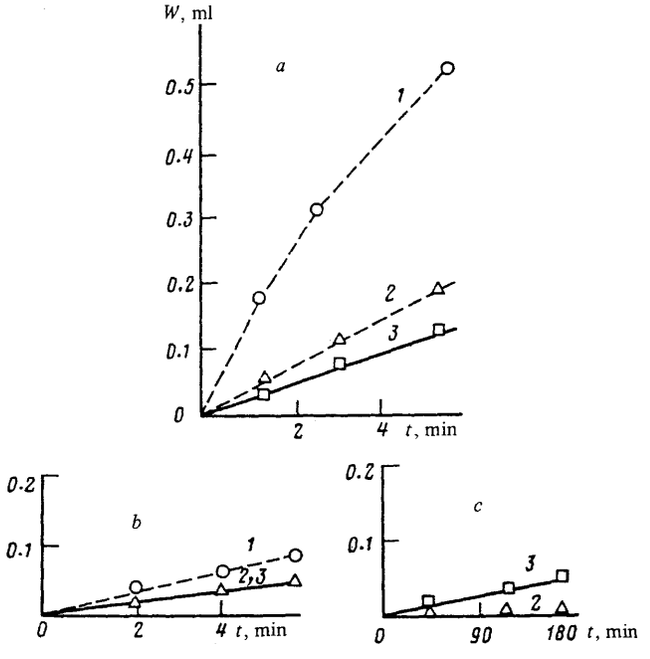



Figure 6. Hydrogenation of buta-1,3-diene on $Mo_2/Al_2O_3$ (*a*), $Mo/Al_2O_3$ (*b*), and the impregnated catalyst based on $(NH_4)_2$. $.MoO_4$ (*c*); molybdenum content (atoms): *a*) and *b*) $5.37 \times 10^{18}$; *c*) $3.16 \times 10^{19}$; 1) but-1-ene; 2) *trans*-but-2-ene; 3) *cis*-but-2-ene ($p_{C_4H_8} : p_{H_2} = 2:1$; 0 °C).[83]

An even greater difference has been obtained in the study of the catalytic activities of the mono- and di-nuclear centres based on the allyl complexes of molybdenum immobilised on the surfaces of aluminium and silicon oxides in the hydrogenation of ethylene (Fig.7).[83] It is of interest that, whereas no differences between the activities of the mono- and di-nuclear centres were observed on $Al_2O_3$, on $SiO_2$ only the immobilised dinuclear complexes were activie. The influence of the nature of the carrier is difficult to explain in this instance. The possible causes are the conversion of the dinuclear complexes into the monomeric form on the surface of $Al_2O_3$ and the lack of a difference between the structures of the mono- and di-nuclear centres. The significantly higher activity of the catalyst based on $Al_2O_3$ is also noteworthy.

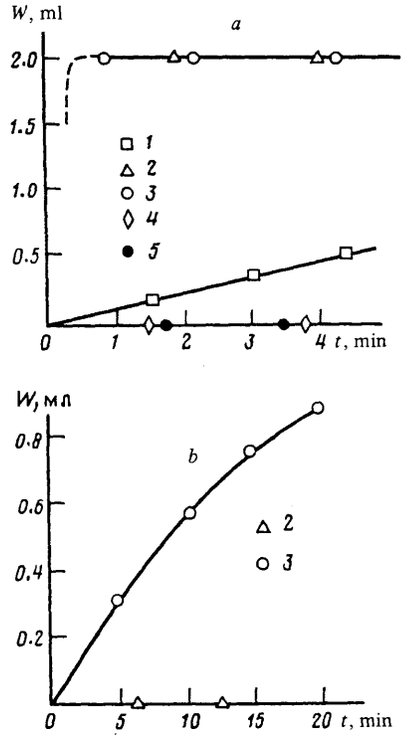



Figure 7. The influence of the structure of the surface centres formed in the oxidation-reduction treatment of the complexes $Mo(\pi\text{-}C_3H_5)_4$ and $Mo_2(\pi\text{-}C_3H_5)_4$, immobilised on $Al_2O_3$ and $SiO_2$, on the yield of ethane in the ethylene hydrogenation reaction ($p_{H_2} = 48$ mmHg; $p_{C_2H_4} = 12$ mmHg). Reaction conditions: *a*) for $TMC/Al_2O_3$, temperature 73 °C, sample size 0.1 g; *b*) for $TMC/SiO_2$, temperature 20 °C, sample size 0.28 g; 1) reduced impregnated catalyst based on $(NH_4)_2MoO_4$; 2) $(|\text{-}O)_2Mo$; 3) $[(|\text{-}O)_2Mo]_2$; 4) $[(|\text{-}O)_2Mo{=}O]_2$; 5) $(|\text{-}O)_2Mo{=}O$.[83]

Thus the nuclearity and the skeleton of the immobilised centre can be frequently preserved in the heterogenisation of transition metal complexes on mineral carriers. However, this does not guarantee that the immobilised structures remain unchanged under these conditions of the catalytic reaction. Unfortunately, very little attention has been devoted to this question in the literature.

## V. THE "ASSEMBLY" OF CLUSTER CENTRES ON THE SURFACES OF CARRIERS

All the methods of synthesis of cluster and polynuclear heterogeneous catalysts described above are based on the same procedure for the immobilisation of the complex obtained beforehand and containing several metal atoms. However, catalysts containing centres with a higher nuclearity can be synthesised also in a different way—from mononuclear complexes, i.e. by "assembling" the cluster or polynuclear active centres directly on the carrier surface.

Two main trends in the application of this method of synthesis of heterogeneous metal complex catalysts have come to be most widely used at the present time. The first may be referred to as the method of statistical assembly and the second the method of programmed assembly on the surface. The first method consists in the preliminary immobilisation on the carrier surface of mononuclear centres which can be converted by further chemical treatment into polynuclear formations stable under given conditions. Naturally, when this method is employed, the structure of the active centre is unknown and the species formed are non-uniform as regards size. This is caused by the statistical nature of the process involving the formation of the structure of the centres and the energetic and geometrical non-uniformity of the carrier surface.

The method of programmed assembly on the surface involves a series of consecutive chemical reactions leading to an increase in the complexity of the structures of the immobilised mononuclear complexes. In this case the degree of uncertainty in the structures of the centres formed on the surface is diminished but the element of uncertainty persists, because the number of different types of centre which may be superimposed on the surface is equal to the number of stages of the reaction occurring on the surface.

Examples of the employment of these two varieties of the surface assembly methods for the synthesis of polynuclear, cluster, and highly dispersed metallic catalysts are presented below. We may note that it is difficult to draw a clear-cut boundary between these types of catalysts, at any rate so long as the particle size does not exceed 30–50 Å.

### 1. Statistical Assembly

The statistical method of surface assembly of highly dispersed metallic catalysts consists in the preliminary immobilisation on the carrier surface of mononuclear complexes (for example, π-allyl complexes) which are reduced with hydrogen at elevated temperatures:

$$\left|\!-\mathrm{OH}\xrightarrow[-\mathrm{HL}]{\mathrm{ML}_n}\left|\!-\mathrm{OML}_{n-1}\xrightarrow{\mathrm{H_2}}\right.\right.\text{microcrystallites of the dispersed metal on the carrier surface.}$$

This method of synthesis of the highly dispersed catalyst as a result of the preliminary heterogenisation of π-allyl complexes of transition metals on $SiO_2$ and $Al_2O_3$ has been developed and studied in detail at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences.[2]

After the reduction of the immobilised π-allyl complexes of nickel, palladium, and platinum, it was suggested that the atomically dispersed metallic phase be produced on the surface. However, the low energy of the migration of atoms on the carrier surface (12.6 kJ $mol^{-1}$), which, amounts to half the energy of the interaction with the surface according to Anderson,[84] prevents the aggregation of metal atoms. The stabilisation of the highly dispersed state is achieved as a result of the preliminary immobilisation of Group VI metal ions in low oxidation states on the surface.[85,86] These atoms serve as "energy traps" and prevent the migration and the increase in the size of the surface particles as a result of the high energy of the $M^{VIII}$–$M^{VI}$ bond. It has been noted[87] that the increase in the interaction energy to 84 kJ $mol^{-1}$ increases the probability of the localisation of the surface atoms by a factor of $10^4$. The metal–metal bond energies in different complexes have been published;[88] these data make it possible to limit the range of atoms whose hydrogenation would promote the stabilisation of the state of the catalytic active centres based on noble and certain transition metals corresponding to the maximum degree of dispersion.

A method has been developed[89,90] for the preparation of highly dispersed palladium and platinum catalysts stabilised by the doubly charged molybdenum and tungsten ions previously immobilised:

$$2\left(\left|\!-\mathrm{OH}\right.\right)+\mathrm{MR_4}\rightarrow\left(\left|\!-\mathrm{O}\right.\right)_2\mathrm{MR_2}\xrightarrow[\mathrm{H_2}]{500\text{–}600^\circ\mathrm{C}}\left(\left|\!-\mathrm{O}\right.\right)_2\mathrm{M}\rightarrow$$

$$\rightarrow\xrightarrow{1)\ \mathrm{PtR_2};\ 2)\ \mathrm{H_2}}\begin{cases}\longrightarrow \underline{\mathrm{M_xPt_n}}\ (\mathrm{I})\ ;\\ \longrightarrow \left|\!\begin{matrix}-\mathrm{O}\\-\mathrm{O}\end{matrix}\right\rangle\mathrm{M}\!-\!\mathrm{Pt}_n\ (\mathrm{II})\ ;\end{cases}$$

$R=\pi\text{-}C_3H_5$; M=Mo, W.

So far it is difficult to state that one of the proposed structures is preferable.[91]

The catalysts obtained by this method had a series of unusual properties compared with the unmodified molybdenum and tungsten catalysts: (1) a high thermodynamic stability of surface centres over a wide temperature range, which is characterised by the constancy of the ratio O : Pt = 1 (at 300–700 °C) in the chemisorption of oxygen; (2) a higher activity in benzene hydrogenation (by a factor of 2–5) and ethane hydrogenolysis (by a factor of $10^4$) reactions (Table 2); (3) a higher stability of the catalytic activity; (4) a change in the kinetic parameters of the hydrogenolysis of ethane (the activation energy is reduced and the order of the reaction with respect to hydrogen is altered).

**Table 2.** The activity of platinum catalysts in the hydrogenation of benzene (25 °C; $H_2 : C_6H_6 = 8 : 1$; 0.53 MPa).[91]

| Catalyst | $c$, wt.% | $T_r$, °C | $a$, mol $g^{-2}$ | $b$, $s^{-1}$ |
|---|---|---|---|---|
| $Pt/SiO_2$ | 3.5% Pt | 500 | 0.21 | 18 |
| $Pt/SiO_2$ | 3.1% Pt | 700 | 0.18 | 20 |
| $(Mo\div Pt)/SiO_2$ | 1.5% Mo; 4.4% Pt | 500 | 1.20 | 64 |
| $(Mo\div Pt)/SiO_2$ | 1.5% Mo; 4.4% Pt | 500* | 2.00 | 110 |
| $(W\div Pt)/SiO_2$ | 4% W; 2.9% Pt | 700 | 0.80 | 46 |
| $(W\div Pt)/SiO_2$ | 6% W; 3.0% Pt | 700 | 1.25 | 67 |

Notation: $c$ is the content of surface elements, $T_r$ the reduction temperature, $a$ the amount of benzene which has reacted per gram of platinum in 1 h, $b$ the amount of benzene (in moles) which has reacted per mole of the surface platinum atoms in 1 s (the turnover number).

*The catalyst was oxidised before reduction.

The study of platinum catalysts by X-ray photoelectron spectroscopy showed that the presence of a Group VI metal ion with a low charge leads to a redistribution of electron density and the appearance of an electron deficiency at the platinum atom. This entails an increase of the binding energy of the $4f_{7/2}$ level, which can be explained, according to the authors,[87] by the transfer of electrons to the oxygen atoms of the mineral matrix, the molybdenum and tungsten

ions with a low charge playing the role of a bridge. If this interpretation is correct, the active centre should have the structure (II) (see Scheme).

## 2. Programmed Assembly

A novel version of the method of the programmed surface assembly has been developed by Semikolenov and co-workers.[92,93] Its essential feature consists in the controllable growth of the catalytic centre, which is immobilised on $SiO_2$ by means of a chemically modified chelating ligand:

$$\text{Si}\begin{matrix}\diagup\ \text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2\\ \diagdown\ \text{CH}_2\text{CH}(\text{CH}_3)\,\text{CH}_2\text{PPh}_2\end{matrix}\ \left(\left|\text{—Si—P}_2\right.\right):$$

$$\left|\text{—Si—P}_2\xrightarrow[(a)]{\text{Pd(OAc)}_2}\left|\text{—Si—P}_2\text{Pd(OAc)}_2\xrightarrow[(b)]{\text{HCOOH}}\right.\right.$$

$$\rightarrow\left|\text{—Si—P}_2\text{Pd(OCOH)}_2\xrightarrow[-\text{CO}_2,-\text{CO},-\text{H}_2\text{O};(c)]{\text{Pd(OAc)}_2}\left|\text{—Si—P}_2\text{Pd}_2\text{(OAc)}_2\xrightarrow[(b)]{\text{HCOOH}}\right.\right.$$

$$\rightarrow\left|\text{—Si—P}_2\text{Pd}_2\text{(OCOH)}_2\xrightarrow[-\text{CO}_2,-\text{CO},-\text{H}_2\text{O};(c)]{\text{Pd(OAc)}_2}\left|\text{—Si—P}_2\text{Pd}_3\text{(OAc)}_2\right.\right.\ \text{etc.}$$

According to the authors' data, by alternating stages ($b$) and ($c$) several ($n$) times, it is possible to obtain a cluster containing $n + 1$ palladium atoms. In order to regulate the stoichiometry of the interaction and the degree of reduction of the $Pd^{2+}$ ions, the process leading to the assembly of the surface cluster was carried out in the presence of a ligand (the formate ion), which possessed, apart from reducing properties, also the ability to immobilise beforehand a new metal ion on the complex already immobilised, as a result of the formation of bridge bonds.

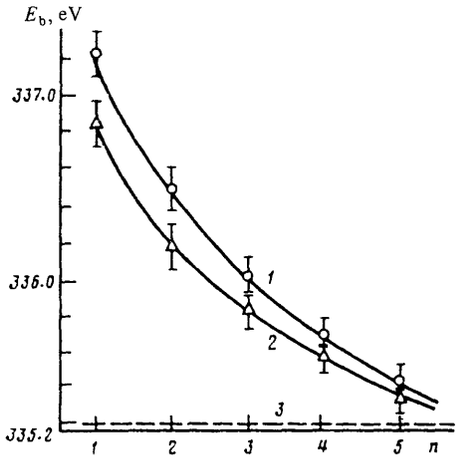



Figure 8. Dependence of the binding energy of the electrons of the Pd atom in the $3d_{5/2}$ level on the number of Pd atoms in the cluster: 1) initial $\left|\text{—P}_2\text{Pd}n(\text{OCHQ})_2\right.$ specimens; 2) the same specimens heated *in vacuo* at 110 °C for 1 h; 3) metallic palladium foil.[92]

The successive formation of surface polynuclear structures with a nuclearity varying from 2 to 5 is demonstrated by the parallel decrease of the binding energy of the electrons in the $3d_{5/2}$ level and the increase of the number of palladium atoms immobilised on the surface of the matrix (Fig. 8).

We may note that the binding energy of the electrons in the $3d_{5/2}$ level for a pentanuclear cluster is very close to the binding energy of the electrons in the same level for the compact metal.

The catalytic properties of the cluster palladium catalysts with $1 \leqslant n \leqslant 5$ have been investigated in the cyclopentadiene hydrogenation reaction and in Zelinskii's irreversible catalytic reaction. The dependence of the catalytic activity on $n$ has been demonstrated. Specimens with $n = 1$ or 2 did not exhibit activity in the disproportionation of cyclohexene. It is extremely probably that the surface of these catalysts contains no palladium microcrystals, because it is known that palladium on $SiO_2$ is an active catalyst in this reaction. For $n = 3$–5, cyclohexene is converted into cyclohexane and benzene with a high yield (Fig. 9). In the cyclopentadienes hydrogenation reaction the catalysts containing monatomic centres were inactive.

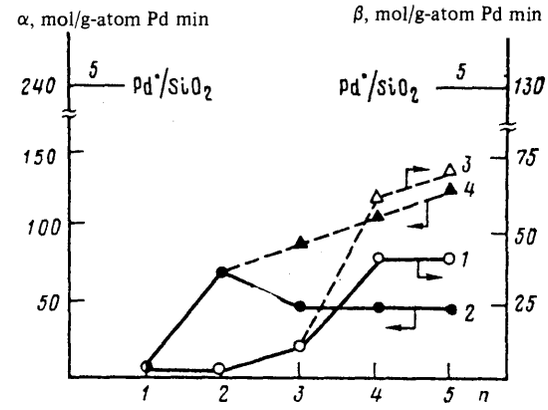



Figure 9. The influence of the nuclearities $n$ of the palladium clusters on their catalytic properties: 1) disproportionation of cyclohexene (β); 2) hydrogenation of cyclopentadiene (α); 3) and 4) calculated dependences of the catalytic activity in the same reactions respectively plotted on the assumption that the active centres for the disproportionation and hydrogenation reactions are the $Pd_3$ and $Pd_2$ fragments respectively; 5) the level of activity of the impregnated $Pd/SiO_2$ catalyst in the same reactions.[93]

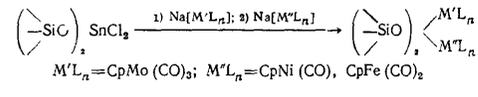
The results of the above studies[92,93] enabled the authors to conclude that the reactions considered proceed only on active centres with a definite structure: the hydrogenation reaction takes place on a diatomic active centre, whereas the cyclohexene disproportionation reaction occurs on a triatomic centre. These conclusions are consistent with the principle of structural correspondence in the multiplet theory of catalysis, to which this composition of the centres for the above reactions corresponds precisely.

Yet another version of the surface assembly method consists of the following operations:[94,95]

$$\left|\text{—OH} + \text{SnCl}_4 \rightarrow \left(\left|\text{—O}\right.\right)_2\text{SnCl}_2\xrightarrow{a\ \text{NaML}_n}\left(\left|\text{—O}\right.\right)_2\text{SnCl}_x(\text{ML}_n)_{2-x}\right.$$

$\text{ML}_n$=CpCr(CO)$_3$, Cr(CO)$_5$, CpMo(CO)$_3$, CpW(CO)$_3$, CpNi(CO); $x = 0, 1$ .

The same approach can be used to synthesise heteroatomic dinuclear complexes:[96]

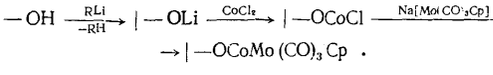


$M'L_n$=CpMo(CO)$_3$; $M''L_n$=CpNi(CO), CpFe(CO)$_2$

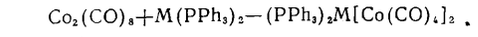
The Group IV non-transition element fulfills several functions: (1) it abolishes the non-uniformity of the carrier surface; (2) it serves as an "anchoring microsupport" for the transition metal atom (the fairly high $M^{VIII}$–$M^{IV}$ bond energy, amounting to 220–300 kJ mol$^{-1}$, gives rise to the hope that the atomically disperse metallic phase will be stable even under the conditions of a fairly high surface concentration of the complex); (3) it modifies the properties of the transition metal; (4) it makes it possible to obtain both homonuclear and heteronuclear immobilised active centres of different nuclearity.

It is noteworthy that this version of the surface assembly method also does not allow the preparation of a sufficiently homogeneous set of active centres on the surface. Thus, in the synthesis of heteronuclear dinuclear complexes, homonuclear as well as heteronuclear active centres may be formed on the surface. Furthermore, mononuclear active centres will persist on the surface, particularly at sites to which access is difficult (for example, within the narrow pores of the carriers). All these factors subsequently introduce an ambiguity into the interpretation of the results obtained. Despite these remarks, one should note that the required active centres are mainly formed on the surface, which is indicated by the almost complete identity of the infrared spectra of the heterogenised complexes and their low-molecular-weight analogues.[97]

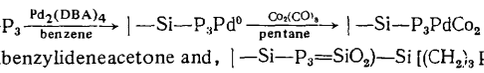
The possibility of employing an analogous approach to the synthesis of heteronuclear surface complexes with a $M^{VI}$–$M^{VIII}$ bond has been demonstrated:[97]

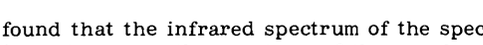


A method of synthesis of bimetallic cluster catalysts has been proposed by Ermakov et al.[98] It is based on the idea of the oxidative addition of a zerovalent palladium complex to the Co–Co bond by analogy with the reaction considered in the book of Nesmeyanov and Kocheshkov:[99]



The heterogeneous catalyst was synthesised in accordance with the scheme



DBA = dibenzylideneacetone and, 

It was found that the infrared spectrum of the specimen obtained is analogous to the spectrum of the complex ($PPh_2$.$CH_2CH_2PPh_2$)Pd[Co(CO)$_4$]$_2$.[100] Together with the results of elemental analysis, these data show that the ratios P : Pd : Co = 3 : 1 : 2, and the results of the study of the heterogenised homonuclear palladium complex $Pd_2(DBA)_4$ and $Co_2(CO)_8$ on the analogous phosphinated $SiO_2$ [101,102] enabled the authors to suggest the formation of the heteronuclear complex |–Si–$P_3$Pd$Co_2$(CO)$_x$, where $x$ = 6–8.

The heteronuclear HMC exhibits an appreciable activity in the hydroformylation of propene even at 40–60 °C, i.e. under conditions where homonuclear HMC are almost inactive. In the course of the reaction the activity of the heteronuclear catalyst fell and the relative yield of the products with the normal structure increased. Thus the introduction of palladium into the composition of the phosphine cobalt carbonyl complex leads to the appearance of a synergistic effect, which is most pronounced at 40–60 °C.

The heterogenisation of the mononuclear iridium complex [Ir(CO)$_2$ (*p*-toluidine) Cl] on polystyrene containing phosphine and diphosphine groups (DIOP) in the presence of zinc leads to the formation of surface clusters.[103–106] Thus the complex containing one phosphine group is formed on polystyrene with phosphine groups in the presence of a low phosphorus content (0.69 wt.%); at higher phosphorus concentrations (1.28 wt.%) the cluster centres linked to the carrier surface via monodentate and chelate bonds are superimposed. On polystyrene containing diphosphine groups, a set of surface compounds is produced. At a low phosphorus concentration in the polymer, |–DIOP[$Ir_4(CO)_{11}$]$_2$ is formed. With increase in the phosphorus concentration, the diphosphine groups begin to behave as chelating ligands and the surface complexes |–DIOP[$Ir_4(CO)_{10}$] are produced. All the immobilised cluster structures exhibit a fairly stable activity in the hydrogenation of ethylene and cyclohexene under mild conditions (40 °C, $10^5$ N m$^{-2}$). Thus, under the reaction conditions mentioned above, the turnover number on the catalyst formed after the heat treatment of |–$PPh_2$.$Ir_4(CO)_{11}$ at 80 °C in helium was 5000. Heat treatment at higher temperatures (120 °C) leads to complete decarbonylation, aggregation of the metal, and an appreciable decrease in catalytic activity.[103,104]

The procedure examined above has been used[107] for the assembly of an iridium cluster on the surface of $SiO_2$ modified by phosphine groups. The reaction was carried out under the conditions of the synthesis of a cluster having the composition [$Ir_4(CO)_nPPh_3$] from the low-molecular-weight complex [Ir(CO)$_2$(*p*-toluidine) Cl] at 90 °C and a 5 atm CO pressure.[108] The authors suggested that the surface phosphine groups play the role of a monodentate ligand.[107]

After decarbonylation, the tetrairidium cluster heterogenised on $SiO_2$ proved to be active in the hydrogenation of ethylene at 30–90 °C. On the basis of the data obtained by Studer and Schrader,[107] one may postulate that the structure of the cluster breaks down in the course of the preliminary treatment and catalysis, and that the reaction proceeds on metallic microcrystals.

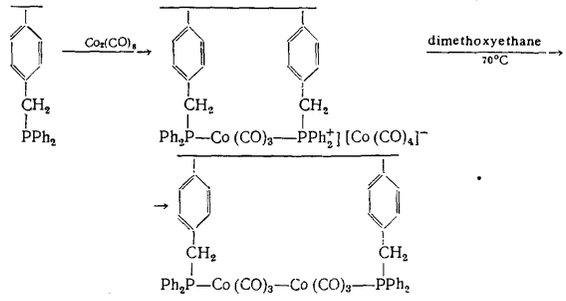
## VI. HETEROGENISATION OF POLYNUCLEAR AND CLUSTER COMPLEXES ON MODIFIED CARRIERS

The application of chemically modified carriers for the heterogenisation of complexes is based on the fact that with their aid it is possible to immobilise complexes on the surface via a chemical reaction specified beforehand, i.e. the use of modified carriers makes it possible to increase the probability of the retention of the initial structure of the transition metal complex. At the same time, chemical modification of the carrier constitutes an additional and frequently fairly laborious stage in the preparation of the catalyst.

### 1. Catalysts on Modified Organic Polymers

The synthesis of a cluster ruthenium catalyst on the surface of the phosphinated styrene–divinylbenzene copolymer, which is active in the hydrogenation of ethylene (52 to 95 °C), has been described.[109]

The heterogeneous metal complex catalyst, active under milder conditions than its homogeneous analogue, has been obtained in accordance with the scheme[110]



The catalyst exhibited a high stability in the hydroformylation reaction: after washing with a solvent, its activity hardly differed from the initial activity. The authors[110] believe that the active centre in this instance is not a dinuclear complex but a mononuclear hydride formed on hydrogenolysis of the Co–Co bond.

The reduction of $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ heterogenised on phosphinated polystyrene yielded an active metallic catalyst for the hydrogenation of arenes at room temperature under normal pressure.[111,112] In contrast to the industrial $Rh/Al_2O_3$ catalyst, the rhodium deposited on the polymer is in a more dispersed state. The authors quote data concerning the extraction of rhodium from the catalyst with the aid of CO as evidence in support of this hypothesis. When the polymer catalyst is treated with carbon monoxide, it is possible to regenerate 50% of the rhodium, while the metal is hardly removed from the $Al_2O_3$ surface.[113]

It has been shown[114,115] that the olefin hydrogenation catalyst obtained by the heterogenisation of $Rh_6(CO)_{16}$ on phosphinated polystyrene contains no carbonyl ligands and the surface phosphine groups play the role of polydentate ligands stabilising the small rhodium clusters on the surface. Carbon monoxide poisons the catalyst and in the presence of traces of oxygen the surface phosphine groups are oxidised, which promotes the agglomeration of rhodium;[115] the activity of the catalyst remains stable at 75 h.

The heterogenisation of $Rh_6(CO)_{16}$ on polystyrene containing *NN*-dimethylbenzylaniline groups led to the synthesis of an active catalyst of the reduction of nitrobenzene and the conversion of water vapour.[116] However, it is somewhat less active and more sensitive to oxygen than its homogeneous analogue.

Studies of the heterogenisation of bimetallic clusters on the surface of phosphinated polystyrene established[117,118] that the clusters $[ClAuOs_3(CO)_{10}Ph_2P-|]$ and $[Co_2Pt_2(CO)_8.(Ph_2P-|)_2]$ with an open structure of the "butterfly" type are active in the hydrogenation of ethylene (<100 °C, $1 \times 10^5$ N $m^{-2}$) in contrast to polymers which contain clusters with a closed tetrahedral structure—for example, $[HAuOs_3(CO)_{10}.Ph_2P-|]$ and $[H_2PtOs_3(CO)_{10}(Ph_2P-|)_2]$.[115] This difference is due to the presence in clusters of the first type of coordination-saturated metal atoms. In order to impart catalytic activity to these clusters, it is essential to rupture the metal–metal bond.

The clusters $[RuPt_2(CO)_5(Pt_2P-|)_3]$ and $[Fe_2Pt(CO)_8.(Ph_2P-|)_2]$ immobilised on phosphinated polystyrene are active in the hydrogenation of ethylene (70–100 °C, $1 \times 10^5$ N $m^{-2}$). However, whereas the first complex is stable (turnover number ~4400), the second decomposes with formation of mononuclear complexes and the metallic phase.[118]

## 2. Catalysts on Modified Silicas

Bilhou et al.[119] heterogenised the rhodium cluster $Rh_6(CO)_{16}$ on the surface of phosphinated silica $\equiv Si(CH_2)_2PPh_2$ (grafting density 1.6 groups per $nm^2$) at room temperature and observed that the cluster is decarbonylated, which is characterised by the disappearance of the absorption bands of the carbonyl groups from the infrared spectrum. Treatment of the specimens with carbon monoxide is accompanied by the appearance of the corresponding bands in the infrared spectrum. This finding as well as the similarity of the stretching vibration frequencies for a series of rhodium carbonyl and phosphinerhodium clusters (Table 6) [Table 6 of Bilhou et al.[119]? (Ed. of Translation)] enabled the authors to suggest that the structure and skeleton of the cluster are retained after its heterogenisation on the mineral carrier.

The partly decarbonylated $Rh_6$ clusters exhibit a low activity in the benzene hydrogenation reaction at room temperature (25 °C). It has also been noted that phosphine-containing clusters, with the exception of that heterogenised on $SiO_2$, exhibit a higher (up to 150 °C) thermal stability than purely carbonyl clusters.

Other results have been obtained from the study of Thornton et al.[120] Two types of $SiO_2$ carriers were used as the matrix for the heterogenisation of the $Rh_6(CO)_{16}$ cluster: $SiO_2$ modified by a phosphine group $-(CH_2)_3PPh_2$ and $SiO_2$ modified by an amine group $-(CH_2)_3NHC_6H_{11}$. The density of the grafting of the functional group on the two carriers was the same (1.1 $nm^{-2}$) and the rhodium contents[119] were 0.24 and 0.66 wt.% respectively.

It has been shown that the interaction of rhodium clusters with aminated $SiO_2$ yields a specimen in the infrared spectrum of which vibrations appear at 2085 and 2003 $cm^{-1}$. These were characterised as symmetric and antisymmetric vibrations of the CO groups of a mononuclear rhodium carbonyl complex containing the $Rh(CO)_2$ fragment. The formula $L_nRh(CO)_2$, where $n$ is the number of amine ligands bound to the surface, may be attributed to this complex. The decarbonylation of the complex diminishes the intensity of the two CO absorption bands mentioned above and leads to the appearance of a new single absorption band at 1943 $cm^{-1}$, which can be assigned[121] to the vibration of the terminal CO group in the complex $L_nRhCO$. The decarbonylation–carbonylation processes

$$L_nRh(CO)_2 \underset{+CO}{\overset{-CO}{\rightleftharpoons}} L_nRhCO$$

are fully reversible up to 157 °C. At this temperature the amine ligand grafted to the surface begins to decompose. The reduction with hydrogen at the temperature above 117 °C is accompanied by the aggregation of the mononuclear rhodium centres, which is indicated by the darkening of the initial brown colour of the specimen and by the appearance in the infrared spectrum of an absorption band at 2020 $cm^{-1}$.

The same band has been observed after the adsorption of CO on the $Rh/Al_2O_3$ deposited catalyst and on thin rhodium films[122,125] (the CO group on 1.5–2.0 nm rhodium crystallites, formed as a result of the agglomeration of rhodium clusters immobilised on phosphinated polystyrene, absorbs at 2045 $cm^{-1}$ [113]). The hypothesis of the formation of the metallic rhodium phase has been confirmed by electron microscopy—the particle size is 1.6–1.7 nm.

During the ethylene hydrogenation reaction at 56 °C, the activity of the rhodium catalyst increased: the degree of conversion rose from 0.3% to 87% during 54 h; the authors explain this finding by the agglomeration of the metal in the course of the catalytic reaction.[120]

A more complex picture is observed in the heterogenisation of $Rh_6(CO)_{16}$ on phosphinated $SiO_2$,[121] but, as in heterogenisation on aminated $SiO_2$, it indicates, according to the authors,[121] the breakdown of the octahedral skeleton. As in the previous case, the surface mononuclear centres agglomerate during the catalytic process, which leads to the

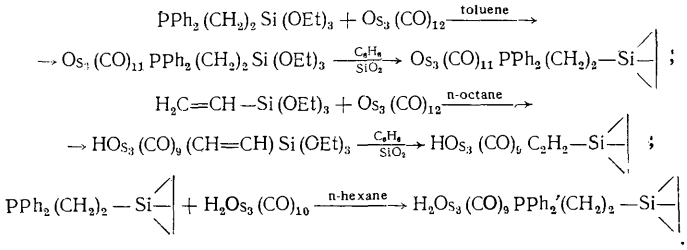
formation of 1.2–1.5 nm crystallites. The process is accelerated in a hydrogen atmosphere and on the phosphine-modified $SiO_2$ the rate of agglomeration of the metal is lower than on aminated $SiO_2$.

The heterogenisation of $Rh_6(CO)_{16}$ on $SiO_2$ modified by phosphine groups has also been investigated.[126,127] If the reaction is carried out at 80 °C in a boiling benzene solution, then, according to the authors, two types of complexes are formed on the surface. One complex contains structures of indefinite nuclearity comprising $Rh^+$ and two terminal CO ligands (in agreement with other data[121,128]). The second complex also consists of metal clusters whose nuclearity is unknown, but, after carbonylation, the infrared spectra of this complex correspond to those of $Ph_6(CO)_{16}/SiO_2$.[19] In the heterogenisation at room temperature hexa-atomic metallic clusters were formed on the surface.[127] The following structure was attributed to their carbonylation products:

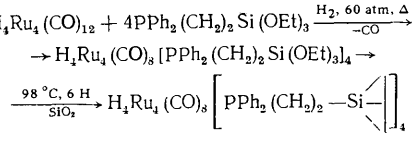


It has been noted that the catalysts obtained from boiling benzene solution are 10 times more active in the hydrogenation of aromatic hydrocarbons than those prepared at room temperature.

Several methods have been described for the heterogenisation of osmium clusters on chemically modified silicas:[128–130]



An analogous approach has been used also in the heterogenisation of the $H_4Ru_4(CO)_{12}$ cluster on $SiO_2$:[131]

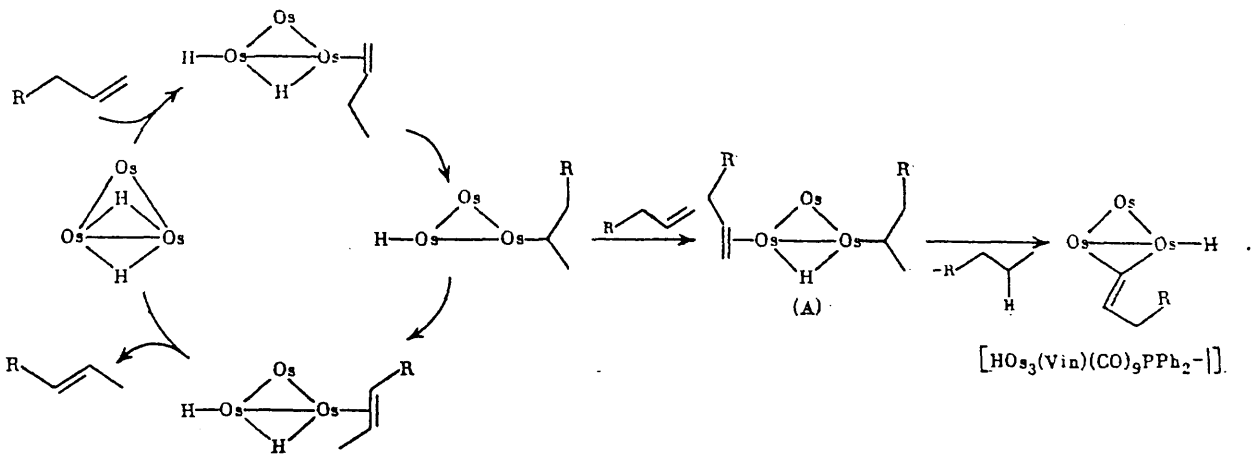


The activity of this catalyst in the ethylene hydrogenation reaction at 70 °C and a $C_2H_4$ and $H_2$ pressure of 100 mmHg is higher by an order of magnitude than the activity of the homogeneous complex $H_4Ru_4(CO)_{12}$ and the $H_4Ru_4(CO)_{12}/SiO_2$ catalyst. According to Doi et al.,[131] the cluster skeleton of the heterogenised complex is retained in the catalytic reaction and the cluster is not washed off into the solution, whereas in the case of $H_4Ru_4(CO)_{12}/SiO_2$ 30–40% of the clusters are transferred to the solution in heptane. This catalyst is regenerated by washing with heptane.

The preparation of heterogenised cluster catalysts by immobilising $[H_2Os_3(CO)_{10}]$ on the surface of $SiO_2$ modified with $[PPh_2(CH_2CH_2)Si(OEt)_3]$ has been reported.[130] An analogous system has been obtained also using phosphinated polystyrene cross-linked by divinylbenzene (3%). The results of an infrared spectroscopic study of the heterogenised clusters and their homogeneous analogues presented in the above communication indicate the retention of the cluster skeleton of the complex on heterogenisation.

The $[H_2Os_3(CO)_{10}]$ cluster is a 46-electron coordination-unsaturated complex, which exhibits a tendency towards conversion into a 48-electron complex in the presence of electron-donating ligands. Consequently, one might have expected that coordination-saturated complexes without catalytic activity would be formed as a result of immobilisation on a phosphinated matrix. A coordination-saturated catalytically inactive complex $[H_2Os_3(CO)_{10}PPh_2/carrier]$ was indeed obtained in the first stage as a result of immobilisation on a phosphinated matrix, which was demonstrated by the similarity of the infrared spectra of the homogeneous and heterogenised compounds.[130] Only after decarbonylation on boiling in hexane was a coordination-unsaturated cluster obtained, exhibiting catalytic activity in the isomerisation of pent-1-ene.

An important feature of the heterogenised clusters compared with the homogeneous analogue $[H_2Os_3(CO)_9PPh_3]$ is their high stability. Thus the homogeneous triosmium cluster decomposed during the reaction with formation of disproportionation products and mononuclear complexes, while the heterogeneous analogues promoted the isomerisation of pent-1-ene with an efficiency equivalent to $10^3$ moles of the olefin per mole of the cluster. The decrease of the activity of the cluster is attributed to the formation of a coordination-saturated complex containing a bridging vinyl ligand. The formation of the 48-electron vinyl cluster is reflected in the mechanism of the isomerisation reaction presented below (the carbonyl and phosphine ligands have been omitted):



It is noteworthy that the activity of the heterogenised triosmium cluster is twice as high as that of another homogenous analogue $[H_2Os_3(CO)_{10}]$. The authors[130] explained this finding by the steric hindrance arising at the stage involving the formation of the product (A), which requires the simultaneous coordination of two olefin molecules and this is responsible for the higher stability of the heterogeneous catalyst. The specific activities of the cluster heterogenised on $SiO_2$ and of its active homogeneous analogue proved to be identical. Bearing in mind the difference between the rate constants for the homogeneous ($k_1 = 0.026 \pm 0.005$ litre $mol^{-1}$ $s^{-1}$) and heterogeneous ($k_2 = 0.08 \pm 0.02$ litre $mol^{-1}$ $s^{-1}$) reactions, the authors[130] suggested that the promoting effect of the phosphine group on the surface is abolished by the influence of the carrier.

The complete analogy between the catalytic behaviour of the heterogeneous cluster and its homogeneous analogue is indicated also by the composition of the reaction products. Thus 19% of hexane and 79% of olefins with inner double bonds are formed in the presence of the triosmium cluster heterogenised on $SiO_2$ (in 45 h at 75 °C and a 4 atm $H_2$ pressure). Analogous results have been obtained[132] under the same conditions in the presence of the $[H_2Os_3(CO)_{10}]$ cluster (19 and 81% respectively).

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As can be seen from the literature data presented in this review, the heterogeneous cluster and polynuclear complex catalysts have attracted the attention of many investigators. However, despite the abundance of studies in this field, so far there have been no reports of qualitatively new results. Nevertheless data have been obtained which suggest that catalytic systems of the class considered are promising. In the first place this applies to cluster HMC for the selective synthesis of alcohols and ethylene glycol by the Fischer–Tropsch reaction.

The experience accumulated in the field of the synthesis, structure, and properties of cluster HMC has shown that these objects undergo changes during preparation, preliminary treatment, and catalysis. In the heterogenisation of cluster and polynuclear complexes, it is therefore necessary to pay special attention to the preservation of their structure.

As an example of an unsuccessful application of the immobilisation method in the preparation of cluster HMC, one may quote the study of Pierantozzi et al.[133] The heterogenisation of the cluster $[H_2FeRu_3(CO)_{13}]$ on phosphinated $SiO_2$ led, according to the authors' results, to the formation of mononuclear centres of the type $[Ru(CO)_4PPh_2-Si\equiv|]$ on the surface. The heterogenisation of the cluster $[Fe_2Pt.(CO)_8(PPh_3)_2]$ on the same carrier was accompanied by the decomposition of the cluster and the aggregation of the metal.

The complexity of the synthesis of the transition metal cluster and polynuclear complexes as well as their instability in the course of the preparation of heterogeneous catalysts necessitate the conclusion that in industrial analysis one should apparently favour the method involving the assembly of the cluster centres on the carrier surface, because relatively simple and accessible initial compounds are immobilised in this process.

For theoretical predictions of catalytic activity, important results can be obtained in the study of the influence of the nuclearity and the geometrical structure of the clusters on the catalytic activity and selectivity of the catalyst. Despite the large number of studies on catalysis by clusters and cluster HMC, many fundamental processes remain open. These include the influence of the nuclearity of the cluster on many-electron and structure-sensitive reactions, the synergistic effect in the above reactions on heteroatomic clusters, and the formation of cluster HMC with an asymmetric activity (both as a result of the presence of chiral ligands and the chirality of the cluster skeleton, arising either as a result of the asymmetry of the metal lattice or as a result of the skeletal asymmetry caused by the form of the cluster[134–137]). Presumably catalysts of the latter type will make it possible to synthesise selectively complex optically active compounds from CO and $H_2$.

During the preparation of the review for the press, a number of other review articles[138–145] and original papers[146–163] devoted to the preparation and application of catalysts based on heterogenised transition metal clusters were published.

Basset and Choplin[138] examined in detail the reactions of cluster compounds on the surfaces of mineral carriers. A mechanism has been proposed for the hydrogenation of olefins on the immobilised cluster $[HOs_3(CO)_{10}(O-|)]$. The results of an investigation of the Fischer–Tropsch reaction in the presence of carbonyl clusters on carriers have been described.[146,163] The reactions of clusters accompanying the Fischer–Tropsch reaction have been considered.

Another study has also been devoted to this topic.[147]

Using the EXAFS method, the interaction of the $[HFe(C).(CO)_{12}]^-$ cluster with the surface of a partly dehydroxylated alumina has been investigated.[148] A study has been made of the activity of the resulting catalyst in the CO and benzene hydrogenation reactions. The processes accompanying the heterogenisation of heteroatomic clusters on mineral carriers have been described in two communications.[149,150]

A simple geometrical model of the kinetics of the aggregation of clusters has been described.[151] Interesting results have been obtained in the study of the properties of catlaysts based on immobilised heteronuclear transition metal clusters.[152,153] Much attention has been devoted to the spectroscopic study of the products of the reaction of the clusters on the surfaces of carriers;[154–156,160,161] special mention should be made of studies[155,160] in which the EXAFS method was used to investigate the immediate environment of the metal ions.

Questions concerning catalysis by immobilised transition metal clusters have been considered at the IInd All-Union Conference on the Chemistry of Clusters (Odessa, May 1985). In addition they have been dealt with in a number of books.[164–166]

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# The Dehydrofluorination of Complexes of Silicon Tetrafluoride with Nitrogen- and Oxygen-containing Donor Ligands

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Data on the dehydrofluorination of complexes of silicon tetrafluoride with N- and O-donor ligands in the absence of a solvent and in benzene, and on the alcoholysis and hydrolysis of silicon tetrafluoride, have been reviewed. The probable mechanism of dehydrofluorination has been discussed.
The bibliography contains 88 references.

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## I. INTRODUCTION

Earlier reviews[1-5] and a monograph[6] summarised data on the properties and structures of the complexes of silicon tetrafluoride with organic bases, but do not give sufficient information on the dehydrofluorination of these complexes. These processes, however, form the basis for the preparation of various fluoro-organosilicon compounds with covalent Si–N and Si–O bonds, of practical interest (fluorosilylamines, hexafluorodisilazanes, oligomeric and polymeric cyclic and linear fluorosilazanes, and alkoxysilanes). Dehydrofluorination reactions are also of undoubted theoretical interest in the study of the relationship between the type of coordination polyhedron of the mixed-ligand fluorocomplex of silicon and the nature of the ligands present. The pioneers in the study of the dehydrofluorination of complexes of silicon tetrafluoride with alkylamines were the group of English workers in London University headed by Aylett, who published their first papers in the mid-sixties. Their success was largely due to their experience with related silicon–nitrogen monomers and polymers.[7,8]

The present review systematises and summarises the results of studies of the dehydrofluorination of complexes of silicon tetrafluoride with nitrogen- and oxygen-containing donor ligands, published up to and including 1984.

## II. THE DEHYDROFLUORINATION OF AMINE COMPLEXES OF SILICON TETRAFLUORIDE IN THE ABSENCE OF A SOLVENT AND IN BENZENE

The high strength of Si–F bonds and the stability of the complexes of silicon tetrafluoride with alkylamines[9] made it necessary to use fairly severe conditions to achieve dehydrofluorination: the complexes, or stoichiometric $SiF_4$–amine mixtures, were heated for a long time at a comparatively high temperature in the presence of special dehydrofluorinating agents, such as $LiAlH_4$, $NaBH_4$, $NaNH_2$, $B_2H_6$, LiH, Na, Al, and Mg.[10-13]

Heating the complexes of $SiF_4$ with secondary or primary amines in the presence of hydrogen fluoride acceptors to 180–220° leads to the removal of one or two molecules of hydrogen fluoride to give tri- and difluorosilylamines or hexafluorodisilazanes:[10,11]

$$SiF_4(R_2NH)_2 \rightarrow R_2NSiF_3 + HF + R_2NH$$
$$SiF_4(R_2NH)_2 \rightarrow (R_2N)_2SiF_2 + 2HF$$
$$2SiF_4(RNH_2)_2 \rightarrow RH(SiF_3)_2 + 2HF + 3RNH_2 .$$

The composition of the dehydrofluorination products is determined not only by the number of hydrocarbon groups in the molecules of the amine ligands but also by the characteristics of the dehydrofluorinating agent used. Thus the reaction of silicon tetrafluoride with dimethylamine in the presence of $LiAlH_4$ or $B_2H_6$ (190–200°) gives dimethylaminotrifluorosilane and bis(dimethylamino)difluorosilane; with Na (25°) or Al (350°), bis(dimethylamino)difluorosilane is obtained; and traces of tris(dimethylamino)fluorosilane $(Me_2N)_3SiF$ are obtained only on prolonged heating (340 h) in the presence of Na (25°). The complexes with ammonia or with primary amines give substituted hexafluorodisilazanes $RN(SiF_3)_2$ (R = H, Me, Et, Ph), unstable aminotrifluorosilanes ($EtNHSiF_3$,[12] $PhNHSiF_3$,[11] or condensed products of the disproportionation of the hexafluorodisilazanes. An increased tendency to form the last compounds was observed for the derivatives $RN(SiF_3)_2$ with R = H, Ph:

$$n\,RN(SiF_3)_2 \begin{cases} \longrightarrow SiF_3NR(SiF_2NR)_{n-1}SiF_3 + (n-1)SiF_4 \\ \longrightarrow (RNSiF_2)_n + n\,SiF_4 \end{cases},$$

The disproportionation of N-alkylhexafluorodisilazanes $RN(SiF_3)_2$ (R = Me, Et) has also been described;[13] the intermediate products $SiF_3NRSiF_2NRSiF_3$ were isolated.

A number of suggestions have been made[11] about the role of different acceptors in the binding of hydrogen fluoride by the dehydrofluorinating agents. Thus $LiAlH_4$ reacts with silicon tetrafluoride and methylamine according to the scheme:

$$4SiF_4 + 2MeNH_2 + LiAlH_4 \rightarrow 2MeN(SiF_3)_2 + LiF + AlF_3 + 4H_2$$

and with secondary amines (R = Me, Et) according to the scheme:

$$(6-2n)SiF_4 + 4R_2NH + LiAlH_4 \rightarrow (6-2n)(R_2N)_nSiF_{4-n} + LiF + AlF_3 + 4H_2 .$$

The thermal decomposition of lithium aluminium hydride in turn is accompanied by the transformations:[14]

$$3LiAlH_4 \rightarrow Li_3AlH_6 + 3H_2 + 2Al$$
$$Li_3AlH_6 \rightarrow 3LiH + {}^3/_2H_2 + Al .$$

The LiH and Al formed have an increased reactivity, and can react with amines and $SiF_4$. The possible reaction of $LiAlH_4$ with amines to give $LiAlH_{4-n}(NR_2)_n$ at increased temperatures is not excluded; under these conditions, the complexes $SiF_4(R_2NH)_2$ can dissociate, and the partial pressure of the amine becomes considerable, and $LiAlH_4$ does not decompose. Dehydrofluorination can evidently take place with the participation of both $LiAlH_4$ and the products of its thermochemical transformations (including organometallic compounds with Li–N[15] and Al–N[11] bonds); however, the contribution of these reactions is not known.

In dehydrofluorination, sodium hydroborate behaves like $LiAlH_4$, but the yield of dehydrofluorination products is slightly lower. The main reaction is complicated by the decomposition of $NaBH_4$ to give borazoles or aminoboranes. When diborane is used as dehydrofluorinating agent, boron trifluoride complexes which are much more stable than the corresponding silicon tetrafluoride derivatives are formed, and the boron trifluoride complexes, for the same reason, are present in the reaction products even in an appreciable excess of $SiF_4$:

$$6SiF_4 + B_2H_6 + (3n + 2)\,R_nNH_{3-n} \rightarrow 3n\,R_nN(SiF_3)_{3-n} + 6H_2 + 2BF_3 \cdot R_nNH_{3-n}.$$

The complexes of primary amines, depending on the type of hydrocarbon group, either give low yields of silazanes (R = Me) or do not form silicon–nitrogen compounds at all (R = H, Pr, Ph). In the latter case, borazoles are formed.

Aluminium, magnesium, and zinc powders, in contact with gaseous mixtures of $SiF_4$ and $MeNH_2$ at increased temperatures, can bind HF:

$$M + nHF + MF_n + n/2\,H_2.$$

The intensification of dehydrofluorination using metals at comparatively high temperatures (>300°) is evidently due to the breakdown of the oxide film on the metal surface.

As already noted, sodium under mild conditions reacts extremely slowly according to the scheme:

$$SiF_4 + n\,Me_2NH + n\,Na \rightarrow (Me_2N)_n\,SiF_{4-n} + n\,NaF + \frac{n}{2}\,H_2$$

An excess of dimethylamine brings about the disproportionation of the initially formed $Me_2NSiF_3$ (base catalysis), so that $(Me_2N)_2SiF_2$ predominates in the dehydrofluorination products:

$$2Me_2NSiF_3 \rightarrow (Me_2N)_2SiF_2 + SiF_4$$

The addition of an excess of methylamine to the reaction gives volatile oligomeric silazanes, which tend to lose silicon tetrafluoride to give cyclosilazanes $(MeNSiF_2)_n$.[11]

With increase in temperature (300–400 °C), more extensive thermochemical transformations of the complexes take place to give polymers containing the $-RNSiF_2-$ fragment. A method for synthesising polymeric silicon–nitrogen compounds by the thermal decomposition of adducts or stoichiometric mixtures of $SiF_4$ with primary or secondary amines in sealed ampoules in the presence of bases such as $NaNH_2$ or $LiAlH_4$ has been patented.[16,17] In a typical example, the thermal decomposition of the complex $SiF_4(MeNH_2)_2$ in the presence of sodamide (350°, 10 h) gives a brown polymer powder:

$$SiF_4(MeNH_2)_2 + 2NaNH_2 \rightarrow 1/n\,(MeNSiF_2)_n + 2NaF + 2NH_3 + MeNH_2.$$

The process can be carried out in two stages: the first stage gives N-methylhexafluorodisilazane (250°, 2 h), which is purified by fractional vacuum distillation and which undergoes further thermal decomposition (100°, 6 h):

$$4SiF_4 + 2MeNH_2 + LiAlH_4 \rightarrow 2MeN(SiF_3)_2 + LiF + AlF_3 + 4H_2$$
$$MeN(SiF_3)_2 \rightarrow SiF_4 + 1/n\,(MeNSiF_2)_n.$$

Selection of the thermal decomposition conditions and the dehydrofluorinating agents makes it possible to vary the mechanical characteristics of the polymeric products from soft to elastic and hard. The polymers with a high molecular mass have a high thermal stability (they do not melt or decompose when heated to 500°), are insoluble in most organic solvents, and are stable to hydrolysis (including the action of aqueous alkali solutions), but decompose in contact with solid alkali.

Published data[10,11,16,17] strengthened the view that in dehydrofluorination it is necessary to use hydrogen fluoride acceptors of basic character. In 1970,[18] however, the ability of silicon tetrafluoride complexes (by themselves or in an excess of $SiF_4$) to undergo "spontaneous dehydrofluorination" was observed. Similar results were obtained in Ref. 19; heating silicon tetrafluoride with trimethylhydrazine or unsymmetrical dimethylhydrazine gave $Me_2NN(Me)SiF_3$ and $Me_2NNHSiF_3$ respectively. The term "spontaneous dehydrofluorination"[18] (that is dehydrofluorination in the absence of special dehydrofluorinating agents) apparently does not fully reflect the essential features of the processes taking place, since no account is taken of the ability of the complexes to act as HF acceptors:

$$SiF_4(R_nNH_{3-n})_2 + 2HF \rightarrow (R_nNH_{4-n})_2SiF_6.$$

Trifluorosilylamines and hexafluorodisilazanes can be obtained by the thermal decomposition of complexes of silicon tetrafluoride with primary and secondary amines in sealed ampoules;[18,20] the presence of an excess of silicon tetrafluoride leads to an increase in the yield of the desired products. The complexes of secondary amines are converted fairly rapidly (1.5–8 h) into the corresponding trifluorosilylamines, and silicon tetrafluoride in turn combines with the dialkylammonium fluoride formed:

$$SiF_4(R_2NH)_2 \rightleftarrows R_2NSiF_3 + R_2NH_2F$$
$$SiF_4 + 2R_2NH_2F \rightleftarrows (R_2NH_2)_2SiF_6.$$

Experiments with the complexes of diethylamine and pyridine proved that the first reaction is reversible.[20] The thermal decomposition of these compounds in a melt gave the corresponding trifluorosilylamines; the original complexes were formed when the products of each reaction were kept at room temperature for several days.

Table 1. Reaction conditions and yields of products in the thermal decomposition of the complexes of silicon tetrafluoride with secondary amines.[20]

| Complex | $t$, °C | $\tau$*, h | Product | Yield, % |
|---|---|---|---|---|
| $SiF_4(Me_2NH)_2$ (liquid) | 175 | 1.5 | $Me_3NSiF_3$ | 52 |
| $SiF_4(Et_2NH)_2$ (solid) | 40 | 21.5 | $Et_3NSiF_3$ | 10 |
| $SiF_4(Et_2NH)_2$ (liquid) | 110–120 | 4.5 | $Et_3NSiF_3$ | 100 |
| $SiF_4(Et_2NH)_2$ (gas) | 175–190 | 7.5 | — | 0 |
| $SiF_4(Pr_2NH)_2$ (solid) | 100 | 3 | $Pr_3NSiF_3$ | 100 |
| $SiF_4(Bu_2NH)_2$ (solid) | 120 | 3.5 | $Bu_3NSiF_3$ | 100 |
| $SiF_4(C_4H_8NH)_2$ (liquid) | 145 | 6 | $C_4H_8NSiF_3$ | 1 |
| $SiF_4(C_5H_{10}NH)_2$ (solid) | 120 | 8 | $C_5H_{10}NSiF_3$ | traces |
| $SiF_4(C_5H_{10}NH)_2$ (liquid) | 175–185 | 3.8 | $C_5H_{10}NSiF_3$ | 16 |

*$\tau$ is the reaction time.

The data in Table 1 show that the yields of trifluorosilylamines increase with increase in the length of the hydrocarbon groups in the amine molecule, and are very low for derivatives of cyclic amines $(CH_2)_nNSiF_3$ ($n$ = 4, 5).

Unfortunately, an objective estimation of the yield of the dehydrofluorination products is difficult, since the time and temperature conditions for different syntheses vary over wide ranges. No justification has been given for the selection of the conditions for carrying out a given reaction.

A combination of differential thermal analysis, differential thermogravimetric analysis, infrared spectroscopy, and elemental analysis made it possible to refine the dehydrofluorination scheme[21–23] and to establish the temperature ranges for achieving it (Table 2) in the thermal decomposition of the complexes of secondary amines:

$$SiF_4(R_2NH)_2(\text{solid}) \rightarrow SiF_4(R_2NH)_2(\text{liquid}) \rightarrow R_2NSiF_3(\text{gas}) + HF(\text{gas}) + R_2NH(\text{gas, liquid})$$

$$\frac{SiF_4(R_2NH)_2(\text{liquid}) + 2HF(\text{gas}) \rightarrow (R_2NH_2)_2SiF_6(\text{liquid})}{3SiF_4(R_2NH)_2(\text{liquid}) \rightarrow 2R_2NSiF_3(\text{gas}) + (R_2NH_2)_2SiF_6(\text{liquid}) + 2R_2NH(\text{gas})}$$

**Table 2.** Thermal analysis of the complexes of silicon tetrafluoride with secondary alkylamines.[22,23]

| Complex | Endothermic effects | | Mass loss, % | | Assignment* |
|---|---|---|---|---|---|
| | $t_0$, °C | $t_{max}$, °C | found | calculated | |
| $SiF_4(Et_2NH)_2$ | 200 | 220 | 15 | 0 | *a* |
| | — | 255 | 65 | 61 | *b* |
| | — | 275 | 100 | 100 | *c* |
| $SiF_4(Bu_2NH)_2$ | 165 | 180 | 7 | 0 | *a* |
| | 220 | 250 | 68 | 63 | *b* |
| | — | 270 | 98 | 100 | *c* |
| $SiF_4 2(C_{10}H_{21})_2NH$ | 160 | 180 | 3 | 0 | *a* |
| | 220 | 235 | 28 | 36 | *b* |
| | — | 275 | 95 | 100 | *c* |
| $SiF_4(C_5H_{10}NH)_2$ | 175 | 210 | 5 | 0 | *a* |
| | — | 265 | 56 | 62 | *b* |
| | — | 280 | 100 | 100 | *c* |
| $SiF_4 2(PhCH_2)_2NH$ | 200 | 215 | 3 | 0 | *a* |
| | 235 | 260 | 52 | 40 | *b* |
| | — | 285 | — | — | *c* |
| | — | 305 | 100 | 100 | *d* |

*$a$ = fusion, $b$ = dehydrofluorination, $c$ = dissociation, $d$ = boiling of the amine.

Thus the silicon tetrafluoride complex itself acts as a dehydrofluorinating agent. The possible use of a silicon tetrafluoride complex as dehydrofluorinating agent was reported earlier.[24]

**Table 3.** Reaction conditions and yields of products in the thermal decomposition of complexes of silicon tetrafluoride with primary amines.[20]

| Complex | $t$, °C | $\tau$, h | Product | Yield, % |
|---|---|---|---|---|
| $SiF_4(MeNH_2)_2$(gas) | 220 | 2.5 | — | 0 |
| $SiF_4(EtNH_2)_2$(gas) | 190—200 | 10 | — | 0 |
| $SiF_4(PrNH_2)_2$(solid) | 200 | 8.2 | $PrN(SiF_3)_2$ | 3 |
| $SiF_4(PrNH_2)_2$(gas) | 190—200 | 10 | — | 0 |
| $SiF_4(BuNH_2)_2$(solid) | 190—200 | 8.2 | $BuN(SiF_3)_2$ | 6 |
| $SiF_4$(i-$BuNH_2)_2$(solid) | 190—200 | 8 | i-$BuN(SiF_3)_2$ | 30 |
| $SiF_4$(i-$BuNH_2)_2$(liquid) | 220—240 | 24 | i-$BuN(SiF_3)_2$ | 75 |
| $SiF_4$(t-$BuNH_2)_2$(solid) | 190—200 | 8 | t-$BuNHSiF_3$ | 60 |
| $SiF_4$(t-$BuNH_2)_2$(liquid) | 220—240 | 24 | t-$BuNHSiF_3$ | 86 |
| $SiF_4$(t-$BuNH_2)_2$(solid) | 180—200 | 12 | — | 0 |

Complexes of primary amines undergo dehydrofluorination in sealed ampoules over a longer period (8–24 h) (Table 3). The process is complicated by the ability of the trifluorosilylamines formed in the first stage to be transformed into the more stable hexafluorodisilazanes:

$$SiF_4(RNH_2)_2 \rightarrow RNHSiF_3 + RNH_3F$$

$$SiF_4 + 2RNHSiF_3 + SiF_4(RNH_2)_2 \rightarrow 2RN(SiF_3)_2 + 2RNH_3F \ .$$

Thermogravimetric data[22,23] (Table 4) give grounds for modifying the scheme for the thermal decomposition of the complexes of primary amines as follows:

$$2SiF_4(RNH_2)_2(\text{solid}) \rightarrow RN(SiF_3)_2(\text{gas}) + 2HF(\text{gas}) + 3RNH_2(\text{gas})$$

$$\frac{SiF_4(RNH_2)_2(\text{solid}) + 2HF(\text{gas}) \rightarrow (RNH_3)_2SiF_6(\text{solid})}{3SiF_4(RNH_2)_2(\text{solid}) \rightarrow RN(SiF_3)_2(\text{gas}) + 3RNH_2(\text{gas}) + (RNH_3)_2SiF_6(\text{solid})} \ .$$

**Table 4.** Thermal analysis of complexes of silicon tetrafluoride with primary alkylamines.[22,23]

| Complex | Endothermic effects | | Mass loss, % | | Assignment |
|---|---|---|---|---|---|
| | $t_0$, °C | $t_{max}$, °C | found | calculated | |
| $SiF_4(EtNH_2)_2$ | 140 | 170 | 53 | 59 | *b* |
| | 250 | 280 | 100 | 100 | *c* |
| $SiF_4(PrNH_2)_2$ | 150 | 178 | 57 | 61 | *b* |
| | 245 | 280 | 100 | 100 | *c* |
| $SiF_4$(i-$PrNH_2)_2$ | 120 | 165 | 55 | 61 | *b* |
| | 250 | 270 | 100 | 100 | *c* |
| $SiF_4(BuNH_2)_2$ | 175 | 195 | 58 | 61 | *b* |
| | 250 | 278 | 100 | 100 | *c* |
| $SiF_4$(i-$BuNH_2)_2$ | 110 | 145 | 57 | 61 | *b* |
| | 230 | 275 | 100 | 100 | *c* |
| $SiF_4(C_7H_{15}NH_2)_2$ | 135 | 165 | 59 | 62 | *b* |
| | 245 | 280 | 100 | 100 | *c* |
| $SiF_4(C_8H_{17}NH_2)_2$ | 140 | 175 | 57 | 62 | *b* |
| | 235 | 280 | 100 | 100 | *c* |
| $SiF_4(PhCH_2NH_2)_2$ | 205 | 230 | 56 | 62 | *b* |
| | 260 | 285 | 100 | 100 | *c* |

The structure of the amine determines not only the yield but also the composition of the dehydrofluorination products.[20] Thus for the complex $SiF_4$(t-$BuNH_2)_2$ containing the bulky t-butyl group, the reaction is complete with the formation of t-$BuNHSiF_4$, whereas the dehydrofluorination of the complexes $SiF_4(BuNH_2)_2$ and $SiF_4$(i-$BuNH_2)_2$ gives N-butylhexafluorodisilazanes. The formation of N-alkylhexafluorodisilazanes is represented as the stepwise replacement of the hydrogen atoms on the nitrogen by trifluorosilyl groups. In the thermal decomposition of the complex $SiF_4$(i-$BuNH_2)_2$ with an excess of $SiF_4$, the products included, in addition to hexafluorodisilazane, an oligomeric oil formed by the disproportionation of the primary product:

$$\text{i-}BuN(SiF_3)_2 \rightarrow SiF_4 + 1/n\,(\text{i-}BuNSiF_2)_n \ .$$

The prolonged thermal decomposition of the complexes $SiF_4(RNH_2)_2$ (R = H, Me, Bu, Ph) at comparatively high temperatures in a nitrogen atmosphere (Table 5)[25] is accompanied by more extensive dehydrofluorination to give stable solid polymeric products: white $(NSiF)_n$, yellow-brown $(MeNSiF_2)_n$, and dark violet $(PhNSiF_2)_n$. Poly-(n-butyldifluorosilazane) was isolated as a high-boiling (350–400°) oligomeric oil and a white waxy non-volatile powder:

$$2SiF_4(NH_3)_2 \rightarrow NH_4F + (NH_4)_2SiF_6 + 1/n\,(NSiF)_n$$

$$2SiF_4(RNH_2)_2 \rightarrow 2RNH_3F + (RNH_3)_2SiF_6 + 1/n\,(RNSiF_2)_n \ .$$

Polymeric fluorosilazanes remain unchanged when heated in a stream of dry nitrogen to 500°, but they can be hydrolysed by strong alkalis. The reaction of dry oxygen with $(NSiF)_n$ at 500° gives silicon dioxide and an unidentified compound containing nitrogen, oxygen, and fluorine.

Table 5. Reaction conditions and the yield of polymeric products in the thermal decomposition of complexes of silicon tetrafluoride with ammonia and primary amines.[25]

| Complex | $t$, °C | $\tau$, h | Product | Yield, % |
|---|---|---|---|---|
| $SiF_4(NH_3)_2$ | 160–170 | 162 | $(NSiF)_n$ | 21 |
| $SiF_4(NH_3)_2$ | 290–310 | 21 | $(NSiF)_n$ | 20 |
| $SiF_4(NH_3)_2$ | 290–310 | 44 | $(NSiF)_n$ | 14 |
| $SiF_4(NH_3)_2$ | 250–280 | 66 | $(NSiF)_n$ | 18 |
| $SiF_4(MeNH_2)_2$ | 250–280 | 84 | $(MeNSiF_2)_n$ | 38 |
| $SiF_4(BuNH_2)_2$ | 250–280 | 72 | $(BuNSiF_2)_n$ | 37 |
| $SiF_4(PhNH_2)_2$ | 250–280 | 72 | $(PhNSiF_2)_n$ | 37 |

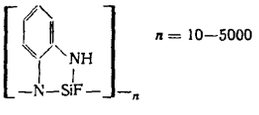
Thermogravimetric, infrared spectroscopic, chemical analysis, and X-ray diffraction data have been used to propose a scheme for the thermal decomposition of the complex $SiF_4(NH_3)_2$ [26] differing from that in Ref. 25. It was shown that the thermal decomposition takes place in stages to give ammonium hexafluorosilicate and a polymer with the composition $(NHSiF_2)_n$ (identified from the similarity of its infrared spectrum to the published spectrum[27]); $HN(SiF_3)_2$ was detected as an intermediate product. Ammonium fluoride was not detected among the thermal decomposition products, as confirmed indirectly in Ref. 28. Thermodynamic calculations for the thermal decomposition of the complex $SiF_4(NH_3)_2$ ($\Delta H^\circ_{decomp} = 2.5$ kJ mole$^{-1}$, $\Delta S_{decomp} =$ 12 kJ mole$^{-1}$ K$^{-1}$) show that the extremely high thermal stability of the complexes is due mainly to kinetic factors.[25]

Harris and Rudner[29,30] were the first to show that the complexes of $SiF_4$ with primary amines can be dehydrofluorinated in the presence of tertiary amines: trimethylamine, triethylamine, or di-isopropylethylamine; trimethylphosphine can also be used.[29] The syntheses were carried out in benzene at room temperature, that is under much milder conditions than dehydrofluorination by thermal decomposition:

$$3SiF_4 + RNH_2 + 2R_3N \rightleftarrows 1/n\,(RNSiF_2)_n + 2\,(R_3NH)\,SiF_5$$

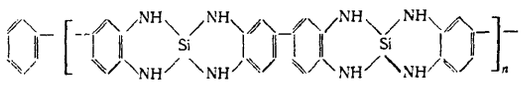
$$(m+1)\,SiF_4 + RNH_2 + 2R_3N \rightleftarrows 1/n\,(RNSiF_2)_n + \frac{2}{m-1}\,(R_3NH)_{m-1}\,Si_nF_{5m+1}^{-(m+1)} .$$

The possibility of the process taking place according to one of the above schemes is determined by the nature of the tertiary amine. The dehydrofluorination of the complexes of methylamine, aniline, and 2-amino-4-chlorotoluene gave mixtures of cyclofluorosilazanes ($n = 3$–5). The oligomer $(MeNSiF_2)_n$ could not be converted[30] into a heat- and water-resistant polymeric product of the type described by Aylett and co-workers.[16,17] The dehydrofluorination of complexes of silicon tetrafluoride with multidentate amines (*o*-phenylenediamine, 3,3',4,4'-tetra-aminobiphenyl) in the presence of triethylamine fairly easily yields the silazane polymers



$n = 10$–5000

and



$n = 2$–1000

which react with a side product of the reaction, trimethylammonium fluorosilicate, to give an oil insoluble in benzene.

Somewhat later, the "spontaneous dehydrofluorination" of complexes of $SiF_4$ with primary and secondary alkylamines under mild conditions was described.[21,23,31,32] Complex formation by silicon tetrafluoride with ethylamine is accompanied by dehydrofluorination even at 25°;[21] in an excess of $SiF_4$, the dehydrofluorination of $SiF_4(EtNH_2)_2$ is complete:

$$SiF_4 + 2EtNH_2 \rightarrow SiF_4(EtNH_2)_2$$

$$2SiF_4(EtNH_2)_2 + SiF_4 \rightarrow EtN(SiF_3)_2 + (EtNH_3)_2SiF_6 .$$

Similarly, in boiling benzene (80°) in the presence of silicon tetrafluoride, the complex $SiF_4(Et_2NH)_2$ undergoes dehydrofluorination according to the scheme:

$$2SiF_4(Et_2NH)_2 + SiF_4 \rightarrow 2Et_2NSiF_3 + (Et_2NH_2)_2SiF_6 .$$

In general, the dehydrofluorination of complexes $SiF_4(RNH_2)_2$ (R represents a group with the normal structure $C_nH_{2n+1}$, $n = 2$–4) is favoured by heating the reaction mixture and an excess of silicon tetrafluoride; with increase in the length of the hydrocarbon group in the amine ligands ($n > 4$), the dehydrofluorination takes place at room temperature and at all $SiF_4$ : amine ratios. Increase in the degree of branching (and hence in the steric effect) of the hydrocarbon group gives the same effect. Thus the dehydrofluorination of the complex $SiF_4(i\text{-}BuNH_2)_2$ takes place at 25° in an excess of the amine. The dehydrofluorination of t-$BuNH_2$ is so vigorous that it is practically impossible to isolate the complex $SiF_4(t\text{-}BuNH_2)_2$ in pure form even with cooling of the reaction medium. Under these conditions, t-butylammonium hexafluorosilicate is precipitated, and t-$BuNHSiF_3$ was identified in the solution by infrared spectroscopy. In boiling benzene, hexafluorodisilazane accumulates in the liquid phase, and is probably produced by the disproportionation of the initially formed t-butyltrifluorosilylamine:

$$2t\text{-}BuNHSiF_3 \rightarrow t\text{-}BuN(SiF_3)_2 + t\text{-}BuNH_2 .$$

As in the thermal decomposition of the complexes of silicon tetrafluoride with the isomeric butylamines,[18,20] the structure of the amine (the steric effect of the substituents on the nitrogen atom, $E_N$ [33]) influences the dehydrofluorination rate and the composition of the reaction products. In particular, the complexes of primary amines with groups having a normal structure, and also isopropylamine and isobutylamine ($E_N = -0.93$ and $-1.10$ respectively) form hexafluorodisilazanes; with t-butylamine, where the substituent has a greater steric effect ($E_N = -1.54$), trifluorosilylamine is formed. It is reasonable to assume that the complexes $SiF_4(RNH_2)_2$ with ligands having a normal structure, in the first stage of the dehydrofluorination, also give unstable $RNHSiF_3$, which rapidly disproportionate to give more stable hexafluorodisilazanes. The stabilisation of products of t-$BuNHSiF_3$ type is most probably due to the sharp increase in interligand interactions in the fragment  [34] on going from t-$RNHSiF_3$ to t-$R_2NSiF_3$.

The dehydrofluorination of the complexes $SiF_4(R_2NH)_2$ (R represents a group with a normal structure $C_nH_{2n+1}$, $n = 2$, 4, 10, 18; R = $CH_2Ph$; $R_2NH = C_5H_{10}NH$) in benzene solution generally takes place under milder conditions than the corresponding transformations of the complexes of primary amines: at room temperature and in an excess of

$SiF_4$, or even at molar ratios $SiF_4$ : amine < 2.[23] As with the complexes of primary amines, increase in the length of the hydrocarbon group R in the ligand molecules intensifies the dehydrofluorination of the complexes $SiF_4(R_2NH)_2$. Thus elemental analysis and infrared spectroscopy show that the reaction of silicon tetrafluoride with dibutylamine in benzene gives a precipitate containing not only $SiF_4(Bu_2NH)$ but also the hexafluorosilicate $(Bu_2NH_2)_2SiF_6$, and in the products of the reaction of $SiF_4$ with $(C_{10}H_{21})_2NH$ and $(C_{18}H_{37})_2NH$, the corresponding dialkylammonium hexafluorosilicates predominate.

The possibility of carrying out the above reactions of "mild" dehydrofluorination (in contrast to the "severe" thermal decomposition processes) is most likely due to the specific properties of benzene as reaction medium.[35] The energy capacity of the benzene molecules[35] gives their large number the function of a buffer; by absorbing the excess energy, liquid benzene prevents elastic collisions of the reagent molecules and increases the probability of reactive collisions, that is it facilitates the formation of activated complexes.

Finally, mention may be made of the problems of identifying dehydrofluorination products; the novel character of the experimental material and the difficulty of isolating the individual compounds, which tend to undergo hydrolysis and disproportionation, complicate their analysis. Nevertheless, spectroscopic methods have been used successfully to identify monomeric, oligomeric, and polymeric fluorosilyl and fluorosilazane derivatives. The strong bands in the infrared spectra of trifluorosilylamines at about 850 $cm^{-1}$ and 960 $cm^{-1}$ are assigned[20] to the symmetric and antisymmetric $\nu(SiF)$ vibrations, and the splitting of the $\nu_{as}$ band into two components (958 $cm^{-1}$ and 980 $cm^{-1}$ for $Me_2NSiF_3$) is attributed to a decrease in the symmetry of the $R_2NSiF_3$ molecule as a result of restricted rotation about the Si–N bond. For trifluorosilylamines, the series of fairly strong bands in the range 1000–1300 $cm^{-1}$ (1051, 1172, and 1221 $cm^{-1}$ for $Et_2NSiF_3$) has been assigned to the CNC fragment stretches.[20,23]

The hexafluorodisilazanes $RN(SiF_3)_2$ give $\nu_{as}(SiF)$ and $\nu_{as}(Si_2N)$ bands in the range 910–1030 $cm^{-1}$, and $\nu_s(SiF)$ bands in the range 790–845 $cm^{-1}$.[11,20,23,36]

For linear and cyclic fluorosilazanes $(RNSiF_2)_n$ and related compounds, the most informative range is 800–1060 $cm^{-1}$, in which the Si–F and Si–N bond vibrations appear. As with the compounds of the previous class, the interpretation of the spectra is complicated by the similarity in the Si–F and Si–N bond stretching frequencies and by overlapping and splitting of the bands. In the spectra of linear fluorosilazanes, the bands have been tentatively assigned as follows: $\nu_{as}(Si_2N)$ 930–980, $\nu_s(Si_2N)$ 600–620 $cm^{-1}$, $\nu_{as}(SiF)$ and $\nu_s(SiF)$ 800–900 $cm^{-1}$.[15,17]

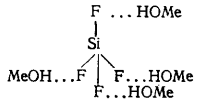
The parameters of the $^1H$ and $^{19}F$ NMR spectra of various trifluorosilylamines, and also $MeN(SiF_3)_2$, $(Me_2N)_2SiF_2$, and $(MeNSiF_2)_3$, have been published.[38,39] The values of the constants $J(^{29}Si–^{19}F)$ are highly characteristic for each type of compound containing the groups $SiF_3$ and $-SiF_2-$ (202–206 Hz and 218–219 Hz respectively).[39]

The parameters of the infrared and $^{19}F$ NMR spectra of "complex" trialkylammonium fluorosilicates with the stoichiometric composition $(R_3NH)_3Si_2F_{11}$ and $(R_3NH)_4Si_3F_{16}$, which are side products of the dehydrofluorination, have been discussed.[30,40–43] In the absence of structural data, these compounds with anions having the empirical formula $Si_nF_{5n+1}^{-(n+1)}$ ($n$ = 2 or 3) can be regarded as double salts $(R_3NH)_2SiF_6.n(R_3NH)SiF_5$ or as salts of polymeric octahedral ions with bridging fluorine atoms. The spectral parameters of the "complex" fluorosilicates (infrared: bands at 720, 790, and 880 $cm^{-1}$ $\nu(SiF)$ and 450 and 480 $cm^{-1}$ $\delta(SiF)$; $^{19}F$ NMR: two singlet signals with chemical shifts of 126–128 p.p.m. and 135–136 p.p.m. relative to $CFCl_3$) do not provide any evidence for a polymeric anion structure with Si–F–Si fragments, and are consistent with the alternative structures $(R_3NH)_2SiF_6.n(R_3NH)SiF_5$. The data in Refs. 38–43 illustrate clearly the value of spectroscopic methods in the identification of dehydrofluorination products. The $^{19}F$ NMR spectra may be particularly useful in the study of the structure and the quantitative estimation of the yields of fluorine-containing products when mixtures of substances difficult to separate are formed.

## III. THE DEHYDROFLUORINATION OF ALCOHOL COMPLEXES OF SILICON TETRAFLUORIDE. THE HYDROLYSIS OF SILICON TETRAFLUORIDE

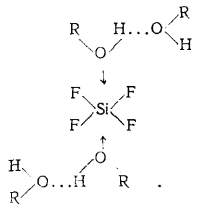
The state of silicon tetrafluoride in solution in aliphatic alcohols, and the question of the possible alcoholysis of $SiF_4$ in these systems, have been the subject of prolonged discussion.[4] Alcohols, which are bases of medium strength, absorb silicon tetrafluoride to give unstable complexes with the composition $SiF_4.4ROH$.[44,45] This stoichiometry of the complexes was confirmed[46] in detailed experiments on the tensimetric titration of silicon tetrafluoride with methanol and of methanol with silicon tetrafluoride. The reported preparation of complexes with the compositions $SiF_4.6MeOH$ and $SiF_4.8MeOH$[47] is apparently erroneous.

A tetrahedral structure has been proposed[46] for the complex $SiF_4.4MeOH$ with four strong hydrogen bonds between fluorine atoms and methanol molecules:




The spectral characteristics (infrared, $^1H$ NMR) of the complex given in Ref. 46, however, can be interpreted as providing evidence for alternative structures. Since silicon tetrafluoride shows appreciable Lewis acidity,[3] its reaction with alcohols only by hydrogen bond formation is unlikely. In fact, analysis of the low-temperature $^{19}F$ NMR spectra of solutions of $SiF_4$ in alcohols ROH (R = Me, Et, Pr, Bu, i-Bu) showed the presence of the complexes *trans*-$SiF_4.(ROH)_2$, *trans*-$SiF_4(ROH)(H_2O)$, and *trans*-$SiF_4(H_2O)_2$.[48,49] The concentrations of the complexes of the last two types were much lower than that of the purely alcohol complexes; the appearance of hydrated forms in the solutions is attributed to dehydration of the alcohols, catalysed by silicon tetrafluoride.[45,46]

$^{19}F$ NMR established the nature of the coordination of only the inner-sphere alcohol ligands forming the $SiF_4O_2$ coordination sphere. Later, however, infrared spectroscopic data for saturated solutions of $SiF_4$ in methanol, ethanol, and isopropyl alcohol[50] confirmed the proposed[48,49] *trans*-octahedral structure of the alcohol complexes. The splitting of the $\nu(CO)$ band into two components in the infrared spectra of alcoholic solutions of silicon tetrafluoride is due to the structural non-equivalence of the alcohol molecules in the complex: two molecules form Si ← O coordinate bonds, and the other two are in the outer sphere. The bonding between the outer-sphere alcohol molecules and the first coordination sphere involves intermolecular hydrogen bonds, where the proton donors are the coordinated alcohol molecules:



It has been claimed[51] that, unlike other silicon tetrahalides, $SiF_4$ in alcoholic solutions does not undergo alcoholysis. Later measurements[46] of the electrical conductivity of methanol solutions of $SiF_4$.MeOH showed that the complex is a very weak electrolyte, that is the inner-sphere alcohol molecules show little tendency to lose protons. The reported[52] rapid dehydrofluorination in the $SiF_4$–MeOH system to give $MeOSiF_3$ and small quantities of $(MeO)_2SiF_2$

$$MeOH+SiF_4\rightarrow MeOSiF_3+HF$$

$$MeOSiF_3+MeOH\rightarrow (MeO)_2SiF_2+HF$$

is somewhat surprising. The reaction conditions were not given,[52] however. Other data[46,48–51] indicate that under ordinary conditions the solvolysis of silicon tetrafluoride in alcohols is not accompanied by appreciable dehydrofluorination, that is the equilibrium

$$SiF_4+n\mathrm{ROH}\rightleftarrows SiF_{4-n}(OR)_n+n\mathrm{HF}$$

is displaced to the left. This is evidently due both to the high strength of the Si–F bond (539–564 kJ $mole^{-1}$) compared with, for example, the Si–Cl (359–380 kJ $mole^{-1}$)[53] and to the inability of alcohols to form stable oxonium complexes with HF. As already noted, the last factor (that is the presence of a hydrogen fluoride acceptor) has a decisive influence on the course of the dehydrofluorination.

The dehydrofluorination of alcohol complexes of silicon tetrafluoride is readily carried out in the presence of strong bases—ammonia or aliphatic amines. Alcohol complexes of $SiF_4$ undergo dehydrofluorination under the influence of trialkylamines to give alkoxysilanes and trialkylammonium fluorosilicates:[30]

$$5SiF_4+4\mathrm{ROH}+4R_3N\rightarrow Si(OR)_4+4(R_3NH)SiF_5 .$$

The bulky di-isopropylethylamine forms a stable pentafluorosilicate, and triethylammonium pentafluorosilicate is stable in benzene and acetonitrile solutions, but when the solvent is removed it loses $SiF_4$ to give the doube salt $(Et_3NH)_2SiF_6.2(Et_3NH)SiF_5$.[43] Similarly, all attempts to isolate trimethylammonium pentafluorosilicate gave a product with the composition $(Me_3NH)_3Si_2F_{11}$, probably the double salt $(Me_3NH)_2SiF_6.(Me_3NH)SiF_5$. To investigate the influence of the nature of the amine on the composition of the dehydrofluorination products, $SiF_4$–EtOH–(primary, secondary, or tertiary amine) systems were studied.[54] The dehydrofluorination in these systems can be described by the equations:

$$3SiF_4+4R_{3-n}NH_n+4\mathrm{EtOH}\rightarrow Si(OEt)_4+2(R_{3-n}NH_{n+1})_2SiF_6$$

$$11SiF_4+12R_3N+12\mathrm{EtOH}\rightarrow 3Si(OEt)_4+4(R_3NH_3)_3Si_2F_{11} .$$

The reaction takes place according to the first scheme when primary and secondary amines are used ($n = 1, 2$); with tertiary amines ($n = 0$), the reaction takes place according to both schemes.

The behaviour of aliphatic diamines,[55,56] 2,2′-iminodi(ethanol), 2,2′,2″-nitrilotri(ethanol),[57] and highly basic N-containing heterocyclic compounds (imidazole, benzimidazole, and its derivatives)[58] in the dehydrofluorination of alcohol complexes of $SiF_4$ is analogous to that of aliphatic monoamines.

A reaction related to the dehydrofluorination of alcohol complexes of silicon tetrafluoride is the hydrolysis of $SiF_4$, usually described[59] by the scheme:

$$2SiF_4+2H_2O\rightarrow SiO_2+SiF_6^{2-}+2H^++2\mathrm{HF} .$$

This is an overall equation, and does not reflect the complex set of equilibria in the $SiF_4$–$H_2O$ system.[4] In acidic silicon–fluoride solutions, various methods have established the existence of the complex $SiF_4(H_2O)_2$,[60–62] whose formation can be regarded as the primary stage of the dehydrofluorination in the reaction of silicon tetrafluoride with water.

Dehydrofluorination in the $SiF_4$–ROH–amine and $SiF_4$–$H_2O$ systems is of interest for the utilisation of silicon tetrafluoride, of which a large tonnage is produced as a waste product in the manufacture of phosphorus fertilisers.[6] According to patents,[63–65] the dehydrofluorination of alcohol complexes takes place according to the scheme:

$$3SiF_4+4\mathrm{ROH}+4NH_3\rightarrow Si(OR)_4+2(NH_4)_2SiF_6 .$$

The yields of tetra-alkoxysilanes are 70–95%. Tetra-alkoxysilanes are used in the synthesis of organosiloxane oligomers and polymers. Silicon tetrafluoride reacts with alcohols in the presence of Zn or Fe;[66] the zinc and iron hexafluorosilicates formed in addition to $Si(OR)_4$ have been proposed for the protection of constructional materials. A method for preparing tetra-alkoxysilanes by the reaction of alcoholic solutions of $SiF_4$ with alkali and alkaline earth metal sulphides, oxides, carbides, chlorides, carbonates, and cyanides has been patented.[67,68] The reaction is described by the scheme:

$$SiF_4+4\mathrm{ROH}+4\mathrm{MA}\rightarrow Si(OR)_4+4\mathrm{MF}+4\mathrm{HA} ,$$

and is accompanied by the formation of the metal fluoride or hexafluorosilicate and the volatile compound HA, for example $H_2S$, $C_2H_2$, etc.

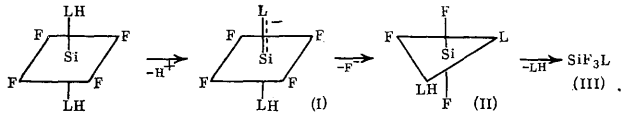
Schemes have now been developed on the industrial scale for utilising silicon tetrafluoride, based on its hydrolysis[69] to give finely dispersed silicon dioxide, $H_2SiF_6$, and $Na_2SiF_6$. The last of these is used on an increasing scale to obtain synthetic cryolite and aluminium fluoride. $SiF_4$ is hydrolysed by water vapour or in the flame obtained by burning hydrogen or a hydrocarbon mixture.[70] Silicon dioxide is separated from the gas mixture on ceramic filters, and the HF is adsorbed on solid sodium fluoride, followed by its thermal regeneration. A patent[71] has proposed a rapid flow method for depositing a film of silicon dioxide on silicon semiconducting devices; a mixture of $SiF_4$, water vapour, and a carrier gas at temperatures of 700–1000 °C is passed over the semiconducting wafer.

## IV. THE MECHANISM OF THE DEHYDROFLUORINATION OF COMPLEXES OF SILICON TETRAFLUORIDE

It has been suggested that the dehydrofluorination of amine and alcohol complexes of silicon tetrafluoride and the hydrolysis of $SiF_4$ should be regarded from the viewpoint of a single mechanism[4,46,49,72] taking account of the specific nature of the bonds in the fluoro-complexes of non-transition elements. Traditional views of the nature of the bonds in compounds of the type $SiF_4X_2$ and $SiF_4X$ [1–3] assume that the 3*d* AO of silicon take part in the bonding and have integral populations. As noted in Ref. 73, however, for five-coordinate fluoro-complexes of silicon it is possible to put forward a counter-argument to practically all the evidence for the participation of the 3*d* AO of silicon in bond formation. According to Williams,[74] the exaggeration of the role

of the outer *nd* AO in the chemistry of non-transition elements results from a historically determined tendency to interpret the octahedral structure of complexes taking account of only two-centre two-electron bonds ($sp^3d^2$ hybridisation of the AO of the central atom), and not delocalised multi-centre bonds. Recently, Musher's alternative hypervalent bond model has been used increasingly to describe the electronic and geometric structure of fluoro-complexes of *p* elements.[75] This model is based on Rundle's postulate[76] that the complex-forming element A with a restricted *ns*, *np* valence basis set, in addition to ordinary two-electron two-centre bonds A–F, also forms three-centre four-electron bonds F–A–F. This model has been used successfully[77–79] to analyse the characteristic features of the structure of silatranes, (aroyloxymethyl)trifluorosilanes with a five-coordinate silicon(IV) atom, and pseudo-octahedral complexes of tin(IV).

By analogy with published data,[79] the structure of the original complexes $SiF_4(LH)_2$ (L = RNH, $R_2N$, RO, HO) with *trans*-orientation of the ligands can be regarded as based on two three-centre hypervalent fragments F–Si–F with almost pure *p* character in the equatorial plane; the axial fragment LH–Si–LH is formed by two ordinary bonds with the participation of $sp_z$-hybrid orbitals of the silicon atom. Dehydrofluorination takes place as a result of the protonic dissociation of one inner-sphere ligand, brought about by the base:




The appearance in the coordination polyhedron of silicon of the π-donor acido-ligand L, which requires the participation of the corresponding equatorial p orbital of silicon for the formation of the π-component of the Si–L bond, leads to a decrease in the strength of the Si–F σ-bonds (*cis*-weakening[80,81]). This favours the removal of one fluoride ion from the coordination sphere of the intermediate (I). The five-coordinate intermediate (II) in turn loses the weakly bonded molecular ligand LH and is transformed into the four-coordinate reaction product (III).

The dehydrofluorination reactions examined in the present review illustrate the configurational lability of fluoro-complexes of silicon(IV), that is the ability of the silicon atom to adopt different coordination numbers (CN) from 4 to 6, depending on the nature of the ligands co-existing in the complex. The phenomenon of configurational lability is due to the orbital-deficient nature of the silicon atom as a non-transition element, and is revealed by the ready decrease in the CN of silicon and increase in the multiplicity of the bond with the ligand as a result of its deprotonation. Dehydrofluorination reactions with a decrease in the CN of the central atom are also extremely typical of the analogous fluoro-complexes of phosphorus(V).[82–86] On the other hand, dehydrofluorination reactions are less characteristic of the fluoro-complexes of the heavier analogues of silicon and phosphorus, that is germanium(IV) and antimony(V).[30,87] The relative stabilisation of the six-coordinate fluoro-complexes of these elements is evidently due to the increase in the valence basis set of the central atoms.[49,88]

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# 1,3-Dipolar Cycloaddition—A General Method of Synthesis of Five-membered Nitrogen-containing Heterocycles with Organoelemental Substituents

O.V.Drygina and A.D.Garnovskii

The review deals with the possibilities and advances in the application of the method of 1,3-dipolar cycloaddition to the synthesis of five-membered nitrogen-containing heterocycles with organoelemental substituents.
The bibliography includes 203 references.

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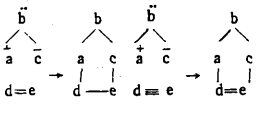
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## I. INTRODUCTION

Heterocyclic compounds with organoelemental substituents play a significant role in modern chemistry: they serve as monomers for the synthesis of heterochain metal-containing oligomers and polymers,[1-5] as ligands for complex formation,[1,2,6,7] and as models for the solution of important theoretical problems, for example in the study of elementotropic processes in the series of five-membered nitrogen-containing heterocycles.[8-14] They are of interest as biologically active compounds[15-19] and are also used for other purposes.[15]

The most widely used methods of synthesis of heterocycles with organoelements substituents are based on the introduction of organometallic fragements into complete heterocyclic systems by direct[20-26] or covalent[27-29] metallation, as a result of the exchange of a halogen for the metal,[21,23,25,26] by the interaction of organometallic derivatives of heterocycles with metal salts,[30-33] via the reaction of the carbonylmetallate anion with halogeno-derivatives of heterocycles,[34-39] etc.

At the same time it is known that heterocycles can be synthesised by constructing the ring from simpler starting materials.[40-44] Methods such as different types of condensations and cyclisations[42-48] or recyclisation[49-51] are therefore applicable also to the synthesis of heterocycles with organoelemental substituents. Such procedures include also the 1,3-dipole addition (1,3-DCA),[52-66] which takes place on addition of two addends: a 1,3-dipole and a dipolarophile. The organoelemental groups can enter into the composition of 1,3-dipoles (diazoalkanes, azides, nitrile oxides, nitrones, nitrile imines, etc.) and dipolarophiles (olefins, acetylenes, nitriles, isonitriles, and heterocumulenes).[56,57,63-66] The general principle governing the construction of five-membered heterocycles by the 1,3-DCA method can be represented as follows on the basis of Huigen's ideas:[52-55]



Thus the type of heterocycle formed in the 1,3-DCA reaction is determined mainly by the nature of the 1,3-dipole ($\overset{+}{a}-\ddot{b}-\bar{c}$), while the dipolarophile (d = e or d ≡ e) determines the degree of saturation of the heterocyclic system. This is why we thought it useful to arrange the description of the data relevant to the present review by taking into account primarily the character of the 1,3-dipole. At the same time one should bear in mind that, when dipolarophiles with heteroatoms are used, the latter can enter into the composition of the heterocycle and hence can alter its type.[56,57,64]

1,3-DCA makes it possible to obtain a wide variety of heterocyclic systems containing the N and O heteroatoms and organoelemental substituents. Since the latter can enter into the composition of the molecules of 1,3-dipole and dipolarophiles, wide prospects arise for the synthesis of N- and C-substituted heterocycles. Whereas the syntheses of heterocycles with organoelemental substituents at the nitrogen atom from complete heterocyclic systems are comparatively easy processes (see, for example, Refs.1, 2, 21, 23, 25, 26), the syntheses of the analogous C-substituted heterocycles give rise to serious difficulties.[67,68] This is why 1,3-DCA is especially useful for the preparation of C-organoelemental derivatives of heterocycles and also of a series of heterocyclic systems with organoelemental substituents in exocyclic fragments which are difficult to obtain.

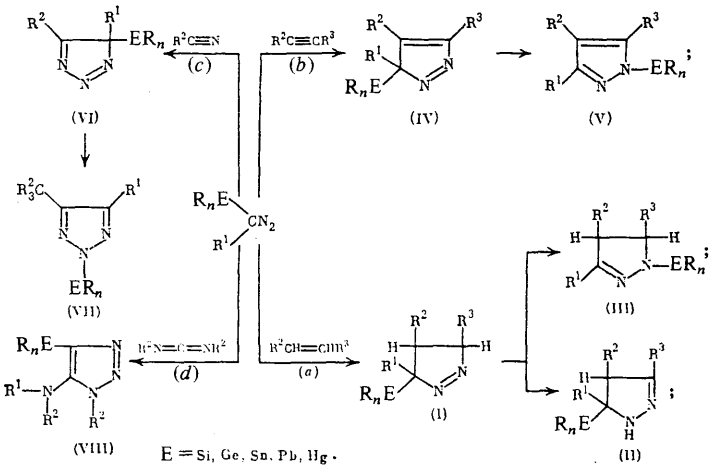
## II. SYNTHESES WITH PARTICIPATION OF DIAZOALKANES

### 1. Synthesis of Heterocycles from Diazoalkanes with Organoelemental Substituents

In order to obtain five-membered nitrogen-containing heterocycles, diazoalkanes with organoelemental substituents are widely used[54-56,63,69,70] (Scheme 1). These make it possible to obtain $R_nEN$- and $R_n$-EC-substituted pyrazolines (on interaction with olefins—pathway a), pyrazolenines and

pyrazoles (in reactions with acetylene—pathway *b*), and triazoles (in reactions with participation of nitriles—pathway *c*, or when nitrogen-containing heterocumulenes, for example carbodiimide, are used as the dipolarophile—pathway *d*).

Scheme 1




*(a) Pyrazolines*

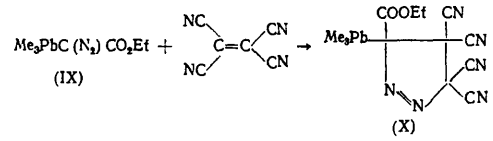
The 1,3-DCA of α-silyldiazoalkanes to acrylonitrile, methyl acrylate, ethyl fumarate, and other dipolarophiles with an activated ethylenic bond has been studied systematically.[63,71-76] The 1,3-DCA reactions considered proceed via intermediate products detected in a whole series of instances. Thus it has been shown from $^1$H NMR spectra[74,76] that the primary products in Scheme 1 (pathway *a*) are 3-organosilyl-$\Delta^1$-pyrazolines (I). Since the majority of $\Delta^1$-pyrazolines readily isomerise to $\Delta^2$-pyrazolines,[77] the isomerisation of the heterocycles (I) leads to compounds (II), if the process is accompanied by the 1,3-transfer of a proton, or to compounds (III) as a result of the 1,3-migration of $R_3Si$. A rearrangement of the first type is characteristic of diazoalkanes $R_3SiC(N_2)R^1$ for $R^1$ = H or Me and one of the second types occurs when $R^1$ = Ph or COOEt.[73,74,76] It has been established for diethyl fumarate[76] that the relative rate of cycloaddition of a diazoalkane diminishes in the sequence

$$\underset{1}{Me_3SiC(N_2)Me} > \underset{2\cdot10^{-2}}{Me_2SiC(N_2)Ph} > \underset{2,5\cdot10^{-3}}{Ph_2SiC(N_2)Me} > \underset{2,5\cdot10^{-4}}{Ph_2SiC(N_2)Ph} > \underset{2,5\cdot10^{-7}}{Me_3SiC(N_2)COOEt}$$

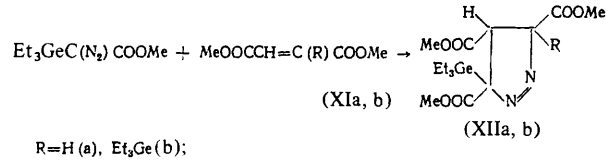
It is believed that the rate of such reactions depends on the degree of $p_\pi, d_\pi$ conjugation of the silicon atoms and the diazo-group in silyl diazoalkanes and on steric factors in the transition state of the cycloaddition reaction.[76]

It has also been shown[74,76] that (1) the 1,3-migration of a hydrogen atom [(I)–(II)] is accelerated by electron-accepting groups $R^3$ and is catalysed by traces of water or amines and (2) that the rate of isomerisation reaction (I) → (II) diminishes as the electron-accepting character of the substituent $R^1$ becomes more pronounced: Me ≥ Ph > COOEt.

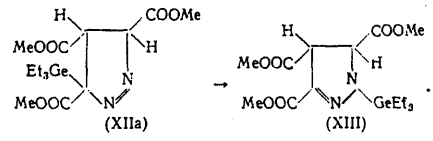
The 1,3-DCA of ethyl trimethylplumbyldiazoacetate (IX) to a wide variety of alkenedipolarophiles, namely acrylonitrile, acetylenedicarboxylic acid, dimethyl maleate, and tetracyanoethylene takes place in accordance with Scheme 1 (pathway *a*).[78] For example, the 1,3-DCA involving tetracyanoethylene (in ether at −20 °C) results in the formation of a derivative of tetracyanotrimethylplumbylpyrazoline (X) in 52% yield:




The 1,3-DCA of methyl triethylgermyldiazoacetate to dimethyl fumarate and 1-triethylgermyl-1,2-ethylenedicarboxylic acids (XIa, c) leads to the $\Delta^1$-pyrazolines (XIIa, b).[79] Among them, the monogermylated adduct (XIIa) isomerises to the $\Delta^2$-pyrazoline (XIII) as a result of the 1,3-migration of the $Et_3Ge$ group. It has been noted that the ester (XIb) is a mixture of the *Z*- and *E*-isomers and that the adduct (XIIb) is therefore also a mixture of isomeric $\Delta^2$-pyrazolines:




R=H (a), $Et_3Ge$ (b);

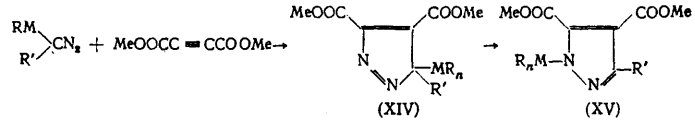



Previously the same authors[80] had obtained bis(triethylgermyl)pyrazolines by the joint thermolysis of ethyl triethylgermyldiazoacetate and ethyl diazoacetate.

*(b) Pyrazolenines and Pyrazoles*

Organoelemental diazomethanes reacting as 1,3-dipoles in interactions involving dipolarophiles containing the acetylenic bond can give rise in the first stage to a pyrazolenine (IV) (Scheme 1, pathway *b*), which is converted into the pyrazole (V) in the course of the sigmatropic rearrangement.

Progress in the development of the methods of synthesis of a wide variety of organometallic diazoalkanes (derivatives of tin,[81] germanium, lead, Group IIB elements,[82] mercury,[83] Group VB elements,[84] thallium,[85] etc.[63,70]) made it possible to introduce them into the 1,3-DCA reaction. For example, the reactions of metallated diazoalkanes $R_nMC(N_2)R'$ with dimethyl acetylenedicarboxylate have been investigated:



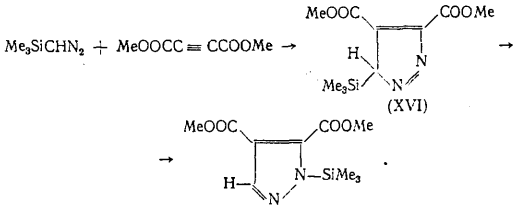

$R_nM$=$Me_2Sn$, $Me_3Pb$, $Me_2Sb$, $Me_3Bi$, MeHg, $HgC(N_2)COOEt$, $HgC(N_2)COMe$; R′=$R_nM$, COOEt, COMe, COPh.

The pyrazolenine (XIV), which readily isomerises to the pyrazole (XV) with 1,3-migration of the $R_nM$ fragments, is formed in the course of the reaction.

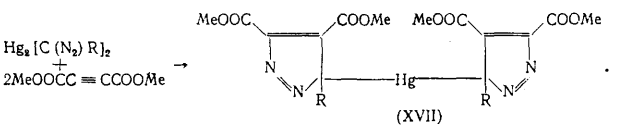
However, it has been found that not all the organometallic diazoalkanes described enter into the 1,3-DCA reaction with acetylenic dipolarophiles: the amount of ionic character of the bond and the bulk of the substituents in the 1,3-dipoles play a significant role in these reactions. Thus, whereas the organoelemental diazoalkanes of the type $R_nEC(N_2)R^1$, where E = Si,[63,70,71,75,86] Sn,[63,87] Pb,[78] Hg,[87] etc.,[63] react with alkynes, the analogous arsenic derivatives do not enter into the 1,3-DCA reaction due to steric hindrance[63] and the

thallium derivative, namely bis(dimethylthallium)diazomethane, does not react because it has an ionic structure.[85]

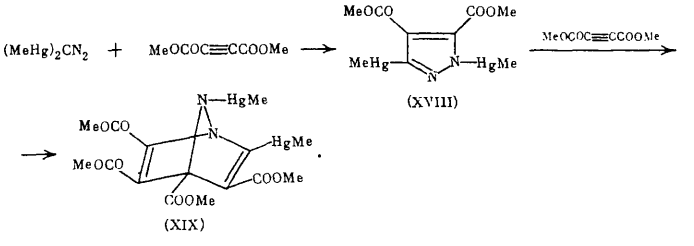
It has also been shown that sigmatropic rearrangements of the type (IV) → (V) are observed also for the 1,3-DCA of $(Me_3Sn)_2CN_2$ and $Me_3SiC(N_2)R$ to MeOOCC≡CCOOMe and are characterised by a decrease of the capacity of the group R for migration in the sequence $Me_3Sn$ > $Me_3Si$ > H > COOEt. For example, the isomerisation of the pyrazolenine (XVI) is accompanied by the migration of $Me_3Si$ and not of a hydrogen atom as had been suggested earlier:[75]



When organoelemental bisdiazoalkanes were involved in the reactions considered above bisheterocyclic systems were isolated. For example, the mercuribisdiazoalkane $Hg[C(N_2)R]_2$, in which R = COOEt or COMe, reacts with dimethyl acetylenedicarboxylate to form the dipyrazoleninemercury derivatives (XVII):[87]



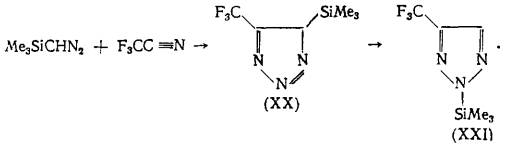
In an analogous reaction bis(methylmercuri)diazomethane is converted into the 1,3-bis(methylmercuri)pyrazole (XVIII), which gives rise to the *CN*-bis(methylmercuri)-derivative of diazanorbornadiene (XIX) on interaction with a second molecule of MeOCOC≡CCOOMe:[87]



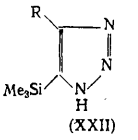
α-Metallated diazoalkanes hardly react with phenylacetylene, diphenylacetylene, sodium acetylenedicarboxylate and bis(trimethylstannyl)acetylene.[63] The causes of such behaviour of the above dipolarophiles are obscure.

*(c) Triazoles*

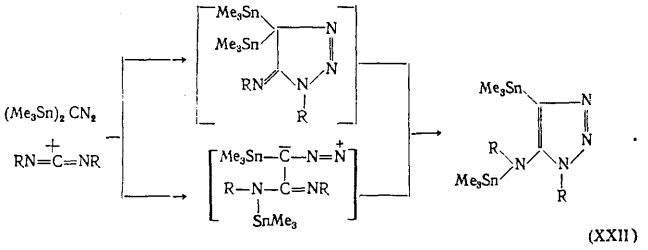
The 1,3-DCA of organoelemental diazoalkanes to nitriles (Scheme 1, pathway *c*) and carbodiimide (Scheme 1, pathway *d*) results in the formation of the triazoles (VI)–(VIII). In particular, it has been established[88] that the interaction of trimethylsilyldiazomethane with trifluoroacetonitrile produces the adduct (XX) which is readily converted into 5-trifluoromethyl-2-trimethylsilyl-1,2,3-triazole (XXI):



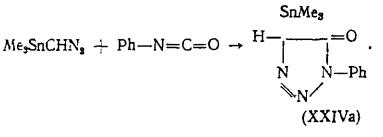
In contrast to the *N*-trimethylsilyltriazoles (XXI) indicated above, the C-substituted triazoles (XXII) with R = Pr, t-Bu, Ph, $PhCH_2$, 1-naphthyl, 2-pyridyl, 1-isoquinolinyl, EtS, and PhO have been obtained via the 1,3-DCA reaction from the lithium salts of trimethylsilyldiazomethane and nitriles.[89–91]



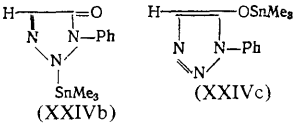
Thus the data presented show that 1,3-DCA can be used for the specific synthesis of *C*- and *N*-organoelemental derivatives of triazoles. Triazole systems with organoelemental substituents are also formed on interaction of organoelemental derivatives of diazomethane with heterocumulene dipolarophiles (Scheme 1, pathway *d*). Thus the dimetallated triazole (XXIII) is formed in the reaction of bis(trimethylstannyl)diazomethane with carbodiimide:[70]



1,3-DCA apparently proceeds analogously in the case of trimethylstannyldiazomethane and phenyl isocyanate.[81] The authors[81] believe that the reaction leads to the formation of the triazolone (XXIVa):



However, a further two isomeric structures, (XXIVb) and (XXIVc), may be proposed for the reaction product taking into account the data presented above, and of these we believe that (XXIVb) is the most probable:



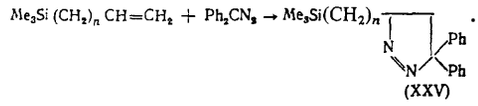
The elucidation of the mechanism of 1,3-DCA with participation of heterocumulene dipolarophiles and of the structure of the products formed therefore requires additional investigation.

## 2. The Synthesis of Heterocycles from Diazoalkanes and Organoelemental Dipolarophiles

Pyrazolines, pyrazolenines, and pyrazoles with organoelemental substituents are formed from diazoalkanes and organoelemental dipolarophiles in the course of 1,3-DCA reactions.[56,57,92–111]

*(a) Pyrazolines*

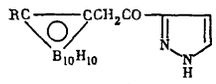
Silylolefins react with diphenyldiazomethane (in proportions of 3 : 1 at +5 °C) to form trimethylsilylpyrazolines (XXV):[92]



(XXV)

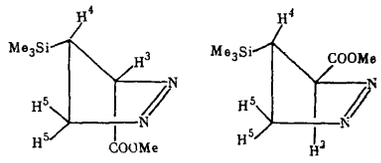
In particular, 3,3-diphenyl-5-trimethylsilyl-$\Delta^1$-pyrazoline (XXV, $n = 0$) has been synthesised in this way. We may note that the same reaction in the presence of copper sulphate as the catalyst leads to silyl derivatives of cyclopropane.

The interaction of carbaboranylmethyl β-chlorovinyl ketones with diazomethane affords the pyrazoles (XXVI).[93]



(XXVI)

The 1,3-DCA of diazoalkanes to alkenes with organoelemental substituents has been studied in detail in relation to the methyl esters of 3-methylsilylpropenoic acid.[94] The *cis*- and *trans*-isomers of $Me_3Si-CH=CHCOOMe$ (XXVIIa, b). obtained by the reduction of $Me_3SiC\equiv CCOOMe$, give rise to high yields of the isomeric *cis*- and *trans*-3-methoxycarbonyl-4-methylsilyl-1-pyrazolines (XXVIIIa, b) on 1,3-DCA to diazomethane (in ether and a nitrogen atmosphere):

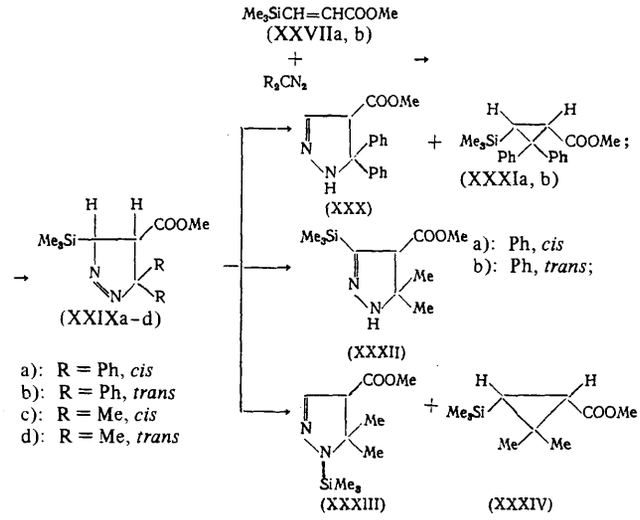


(XXVIIIa) (XXVIIIb)

The pyrazolines (XXVIIIa, b) whose structure has been demonstrated by $^1H$ NMR, subsequently rearrange with elimination of a nitrogen molecule, the migration of the $Me_3Si$ substituent from the C(4) to the C(5) atom of the pyrazoline ring, and the formation of a series of *cis*(*trans*)-isomeric silicon-containing ethylene derivative. The reaction involving monosubstituted diazomethanes proceeds analogously.[94]

The cycloaddition of diphenyldiazomethane to the *cis*-isomer of the methyl ester (XXVIIa) gives rise to *cis*-4-methoxycarbonyl-3,3-diphenyl-5-trimethylsilylpyrazoline (XXIXa) in 71% yield, while its addition to the *trans*-isomer of the methyl ester (XXVIIb) results in the formation of *trans*-4-methoxycarbonyl-3,3-diphenyl-5-trimethylsilyl-1-pyrazoline (XXIXb). Heating of the pyrazoline (XXIXa) in protic solvents leads to disilylation and the formation of compound (XXX), while prolonged thermolysis in boiling hexane produces *cis*- and *trans*-2,2-diphenyl-3-trimethylsilylcyclopropanecarboxylates (XXXIa, b) in proportions of 2 : 3. The thermal stability of the pyrazoline (XXIXa) is higher than that of compound (XXIXb), but it eliminates nitrogen in boiling octane, forming the *cis*- and *trans*-carboxylates (XXXIa, b) in proportions of 1 : 4.

The reaction of the *cis*-isomer of the methyl ester (XXVIIa) with 2-diazopropane leads to the formation of 4-methoxycarbonyl-5,5-dimethyl-3-trimethylsilyl-2-pyrazoline (XXXII) in 75% yield, which has been demonstrated by the $^1H$ NMR spectrum of the reaction mixture before its further treatment. Other results have been obtained for the reaction of 2-diazopropane with the *trans*-isomer of the methyl ester (XXVIIb). In this case analysis by the GLC method demonstrated the presence in the reaction mixture of 4-methoxycarbonyl-5,5-dimethyl-1-trimethylsilyl-2-pyrazoline (XXIII) and the *trans*-cyclopropanecarboxylate (XXXIV) in proportions of 1 : 1. However, the signals which could be assigned to compounds (XXXIII) and (XXXIV) are absent from the $^1H$ NMR spectrum of the above mixture, but signals due to the pyrazoline (XXIXd) are present. The authors point out that, under the GLC conditions, compound (XXIXd) is the starting material in the formation of compounds (XXXIII) and (XXXIV). The dimethylpyrazoline (XXIXd) is sensitive to the action of water, like the diphenylpyrazoline (XXIXa), and when moist 2-diazopropane is employed in this case, the desilylated 4-methoxycarbonyl-5,5-dimethyl-2-pyrazoline is formed in a high yield:



(XXIXa-d)

a): R = Ph, *cis*
b): R = Ph, *trans*
c): R = Me, *cis*
d): R = Me, *trans*

(XXX) (XXXIa, b)

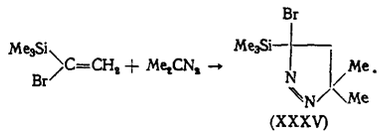
(XXXII)

a): Ph, *cis*
b): Ph, *trans*;

(XXXIII) (XXXIV)

It was then shown that the 1,3-DCA is stereospecific and is sensitive to the nature of the 1,3-dipole, namely to the character of the substituents R, and makes it possible to synthesise specifically the isomeric forms of pyrazolines.

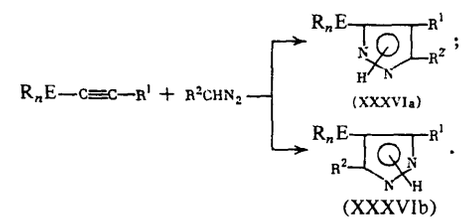
Treatment of an ethereal solution of dimethyldiazomethane with α-bromovinylsilane at 0 °C leads to the formation of 3-bromo-5,5-dimethyl-3-trimethylsilylpyrazoline (XXXV) in 63% yield:[95]



(XXXV)

*(b) Pyrazoles*

The addition of diazoalkanes to acetylenes with organoelemental substituents has been studied fairly completely.[56,57] It proceeds in accordance with the 1,3-DCA principle and leads to the formation of two isomeric pyrazoles (XXXVIa, b):

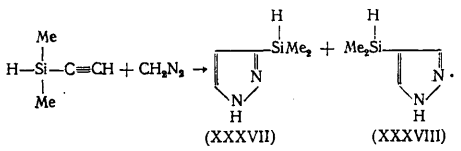


(XXXVIa)

(XXXVIb)

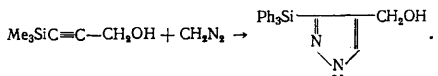
E usually represents Group IV elements (Si, Ge, Sn, and Pb), although similar syntheses of pyrazoles with other organoelemental substituents are known.[56,57] R, $R^1$, and $R^2$ are usually aliphatic or aromatic substituents, $R^1$ representing not only hydrocarbon groups but also a wide variety of functional groups ($CH_2OH$, $-C(=O)P$, etc.). Thus the interaction of diazomethane ($R^2$ = H) and its monosubstituted derivatives ($R^2$ = alkyl or aryl) with trialkyl derivatives of silicon[96,97] or tin[98,99] leads to the formation of pyrazoles containing the substituents $R_3E$ (E = Si or Sn) in the 3- or 5-position.

In the course of its 1,3-DCA to diazomethane in absolute ether at 0–5 °C (three weeks), ethynyldimethylsilane gives rise to a mixture of approximately equal amounts of 3- and 4-dimethylsilylpyrazoles (XXXVII) and (XXXVIII):[100]



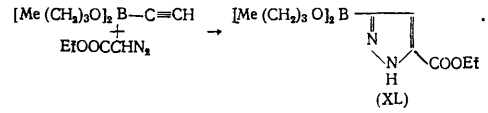
(XXXVII) (XXXVIII)

Triphenylsilylpropargyl alcohols enter into the 1,3-DCA reaction,[99,101] producing mainly compound (XXXIX):



(XXXIX)

Reaction specificity has been observed also in the addition of diazoacetic ester to dibutyl ethynylboronate[102] with formation of a boron-substituted pyrazole (XL):



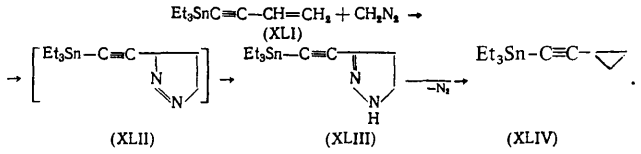
(XL)

Ethyl diazoacetate enters into an analogous reaction with dibutyl ethynylboronate.

The 1,3-DCA reaction with participation of bi- and polyfunctional dipolarophiles is of considerable interest; heterocycles not only with organoelemental but also with active functional groups have been obtained in the course of this process. Polyheterocyclic systems with organoelemental substituents are frequently formed as a result of this type of 1,3-DCA.

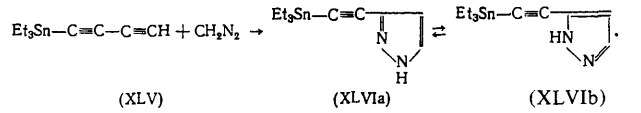
Systematic studies of the competitive reactivities of difunctional dipolarophiles[64,103] have shown that, in the presence of two reaction centres, αβ-unsaturated heteroatomic compounds can react in two ways: with participation of the multiple bond, i.e. [3 + 2]-cycloaddition, or via the heteroatom. Furthermore, it has been established in studies by the same authors that, in the presence of two multiple bonds in the dipolarophile molecule, the most electrophilic of these enters into the 1,3-DCA reaction.[104,105] The data presented above clearly illustrate this behaviour.

Metallated vinylacetylenes combine with diazo-compounds at the more electrophilic double bond with formation of the corresponding pyrazolines. In particular, triethylstannylfinylacetylene (XLI) reacts in this way with diazomethane to form the $\Delta^1$-pyrazoline (XLII), which readily isomerises to $\Delta^2$-pyrazoline (XLIII). On heating to 120 °C, the latter is fully converted into cyclopropyltriethylstannylacetylene (XLIV) with evolution of a nitrogen molecule:



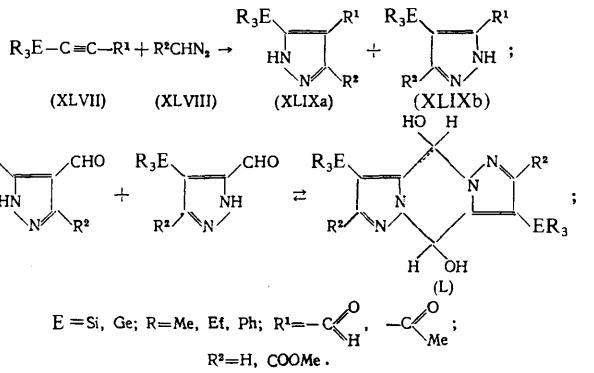
(XLII) (XLIII) (XLIV)

1,3-DCA takes place analogously at the more electrophilic carbon atom of the terminal acetylenic bond in the case of triethylstannyldiacetylene (XLV) with formation of 3(5)-(triethylstannylethynyl)pyrazoles (XLVIa, b):



(XLV) (XLVIa) (XLVIb)

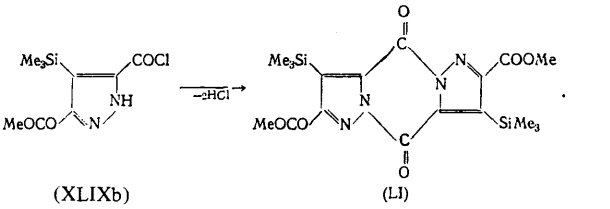
The reactions of triorganylgermanium- or triorganylsilicon-containing carbonyl derivatives (XLVII) with diazoalkanes[106] or with methyl esters of diazoacetic acid (XLVIII)[107–112] lead to the formation of the isomeric pyrazoles (XLIXa, b) and also of the tricyclic hemiaminal (L, $R^1$ = CHO):



(XLVII) (XLVIII) (XLIXa) (XLIXb) (L)

E = Si, Ge; R = Me, Et, Ph; $R^1$ = –C(=O)H, –C(=O)Me; $R^2$ = H, COOMe.

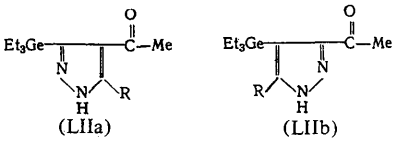
The interaction of trimethylsilylpropiolic acid chloride (XLVII, E = Si, R = Me, R' = COCl) and methyl diazoacetate (XLVIII, $R^2$ = COOMe)[112] proceeds analogously. However, the dioxopiperazine (LI) and not a heminal of type (L) is then formed from the pyrazole (XLIXb) on dehydrohalogenation:



(XLIXb) (LI)

The 1,3-DCA reaction described above proceeds under mild conditions at room temperature or on cooling in absolute ether, albeit over a long period (from 1 to 60 days). The character of the adducts formed, whose structure has been demonstrated on the basis of 1R and $^1$H NMR spectra, and the ratio of the isomeric pyrazoles depend on the substituent $R^2$ in the diazoalkane and on the nature of the solvent.

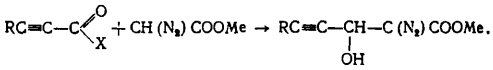
It has been shown[105] that only a mixture of the isomeric pyrazoles (LIIa, b) is formed from methyl triethylgermylethynyl ketone.



(LIIa) (LIIb)

The ratio of the isomers depends on the composition of the 1,3-dipole: an equilibrium mixture of the isomers (LIIa, b) is obtained from diazomethane, in the reaction involving diazoacetic ester the isomer (LIIb) greatly predominates, and in the reaction of diazoacetone the isomer (LIIa) is obtained preferentially.

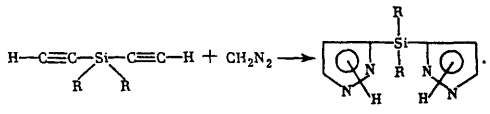
The 1,3-DCA reaction with participation of organoelemental propynals as 1,3-dipoles leads to the formation, apart from pyrazoles, of cyclic hemiaminals (L)[106–110] and also of element-containing diazoesters (LIII) as a result of addition to the aldehyde group:[108]



(LIII)

The nature of the solvent has a significant effect on the content of the dimeric form (L) and the monomeric form (XLIX): according to $^1$H NMR data, the equilibrium in weakly polar solvents (THF, $CHCl_3$, and dioxan) is displaced towards the dimer, while in more polar solvents [MeOH and dimethyl sulphoxide (DMSO)] it is shifted towards the monomeric formylpyrazole.[108,109]

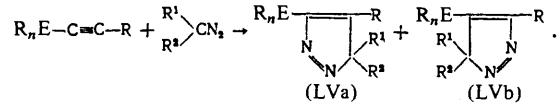
Here we may also note that the 1,3-DCA of diazomethane to bisacetylenic derivatives with equally electrophilic dipolarophile groups, for example, $R_2Si(C{\equiv}CH)_2$, is accompanied by the reaction involving both triple bonds and leads to silylenebispyrazole systems (LIV):[56]



(LIV)

*(c) Pyrazolenines*

The 1,3-DCA method makes it possible to obtain pyrazole isomers which are otherwise difficult to synthesis—the pyrazolenines,[113] their formation being promoted by the use of disubstituted diazo-compounds and disubstituted acetylenes. Thus pyrazolenines have been obtained in the form of two isomers (LVa, b) by the reaction of metallated acetylenes with disubstituted diazoalkanes:[101]



(LVa) (LVb)

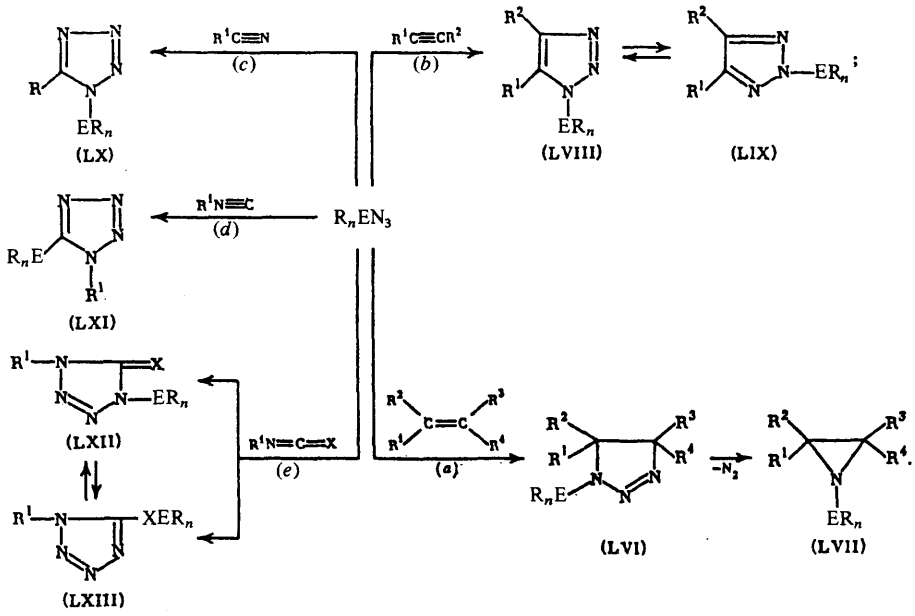
The data presented in Section II suggests the conclusion that 1,3-DCA makes it possible not only to obtain a wide variety of *C*- and *N*-derivatives of pyrazolines, pyrazoles, pyrazolenines, triazoles, and complex polycyclic systems but also to direct the reaction towards the preferential formation of specific isomers.

## III. SYNTHESES WITH PARTICIPATION OF AZIDES

### 1. Syntheses of Heterocycles Based on Organoelemental Azides

The common instances of syntheses based on organoelemental azides are presented in Scheme 2:

Scheme 2

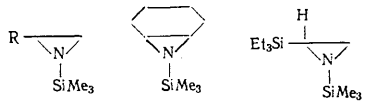


(LXII), (LXIII) X = O, S; E = Cu, Au, Hg, Si, Sn, Pb, Pt, Pd, Ru

*(a) Triazolines and Azirdines*

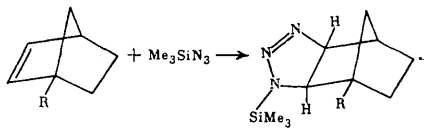
The interaction of organoelemental azides with alkenes (Scheme 2, pathway *a*) leads to the unstable triazolines (LVI), which are converted, as a result of the elimination of a nitrogen molecule, into the N-substituted aziridines (LVII) which are comparatively difficult to obtain.

Thus the interaction of trialkylsilyl azide with the corresponding olefin, which takes place after the reactants have been allowed to stand for a long time (up to 85 days), makes it possible to obtain a series of aziridines (LXIV)–(LXVI),[114] including the formation of the bistrialkylsilyl derivatives (LXVI) from a silylated olefin:



(LXIV) (LXV) (LXVI)

A fairly stable triazoline (LXVII) can be isolated after the interaction of trimethylsilyl azide with a bridge bicyclic olefin:[115]

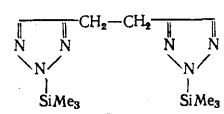


(LXVII)

*(b) Triazoles*

1,3-DCA with participation of organoelemental azides and acetylenic dipolarophiles (Scheme 2, pathway *b*) was first used to obtain organoelemental derivatives of 1,2,3-triazoles by Birkofer and co-workers:[116–120] after prolonged heating of mixtures of trimethylsilyl azide and substituted acetylenes, high yields of *N*-trimethylsilyl-1,2,3-triazoles were obtained. It was established by the method of dipole moments that the $R_3Si$-substituted 1,2,3-triazoles exist in the form of isomers and it has been suggested that the $R_3Si$ substituent migrates rapidly between the N(1) and N(2) atoms of the triazole ring. This was evidently the first case of elementotropism among heterocyclic compounds, which was later demonstrated convincingly in a whole series of tautomeric systems,[7–13] including pyrazole[8,10] and triazole[11,13] derivatives containing organoelemental substituents.

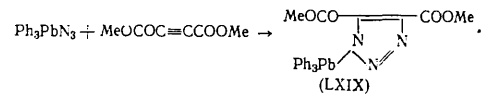
The bisheterocyclic systems (LXVIII) was also synthesised by means of the reactions indicated above; the reaction was carried out in an autoclave at 120–150 °C and the yield of the product was 80%.[119]



(LXVIII)

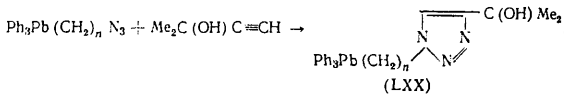
The interaction of trimethylsilyl azide with substituted acetylene RC≡CR′ leads to the formation of 1-trimethylsilylmethyl-4-R-5-R′-1,2,3-triazoles.[121]

Triphenylplumbyl azide,[122–125] was made to react with a large number of olefinic and acetylenic compounds.[126] However, the reaction does not take place with maleic anhydride, dimethyl maleate, ethyl vinyl ether, morpholinocyclopentene, diphenylacetylene, phenylacetylene, propargyl alcohol or 2-methylbut-2-en-2-ol. 4,5-Dimethoxycarbonyl-1-triphenylplumbyl-1,2,3-ditrazole (LXIX) is formed only in the reaction with dimethylacetylenedicarboxylate, which is a very powerful dipolarophile:



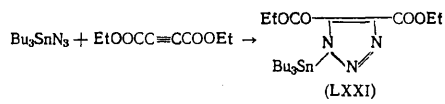
(LXIX)

In contrast to triphenylplumbyl azide, triphenylplumbylalkyl azides readily enter into 1,3-DCA even with weak dipolarophiles such as 2-methylbut-3-en-2-ol, forming the corresponding triazoles (LXX):



(LXX)

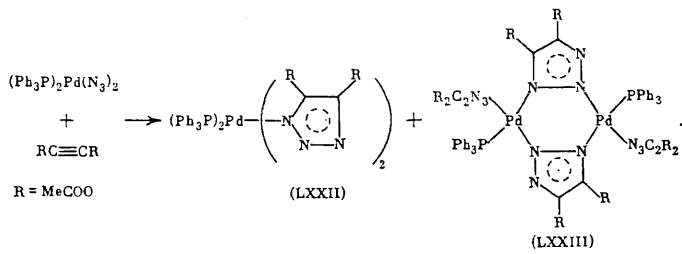
Heterocycles with a N–Sn bond [compounds (LXXI)] can be synthesised from organotin azides and substituted acetylenes as described, for example, by Leijten and van der Kerk:[127]



(LXXI)

We may note that the structures of compounds (LXIX)–(LXXI) quoted in the studies considered above are open to doubt: they have not been demonstrated and, when account is taken of the possibility of the metallotropic N(1)–N(2) migrations of the organoelemental groups, structures of type (LIX) appear to be more probable.

Unusual products are obtained on 1,3-DCA of palladium-substituted organophosphorus azides to dimethyl acetylenedicarboxylate: apart from N-palladium derivatives of the bispyrazoles (LXXII), the highly symmetric dimers (LXXIII) are produced:[128]



(LXXII) (LXXIII)

*(c) Tetrazoles, Tetrazolones, and Their Thio-analogues*

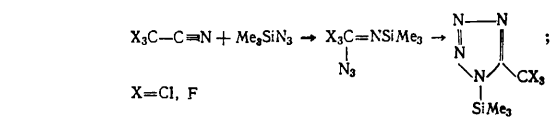
Organoelemental derivatives of the tetrazoles (LX) and (LXI) are formed as a result of the 1,3-DCA of organoelemental azides to nitriles (Scheme 2, pathway *c*) and isonitriles (Scheme 2, pathway *d*).[129–147] The reactions of these azides with heterocumulenes lead to the tetrazolones (LXII) (Scheme 2, pathway *e*) and their thio-analogues.[128,133,135]

Using Scheme 2 (pathways *c*, *d*, and *e*), it is possible to synthesise specifically *N*-substituted [compounds (LX) and (LXII)] or *C*-substituted [compounds (LXI) and (LXIII)] derivatives respectively.

The addition of trimethysilyl azide to benzonitrile takes place in the presence of catalytic amounts of $AlCl_3$ or other Lewis acids.[135]

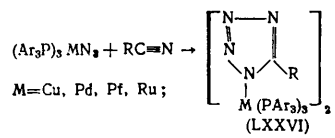
It has been found[136] that trimethylsilyl azide adds to the C≡N bond also in the presence of catalytic amounts of triethylamine. Thus the interaction of $Me_3SiN_3$ with trichloro- or trifluoroacetonitrile with participation of the

above catalyst leads to trihalogenomethyl-1-trimethylsilyltetrazoles (LXXV). It has been shown that aluminium chloride is ineffective in this reaction, since it induces the polymerisation of the nitriles. The 1,3-DCA proceeds in this case via the stage involving the formation of 1-azido-2,2,2-trihalogeno-1-(trimethyl-silylimino)ethanes (LXXIV):



(LXXIV) (LXXV)

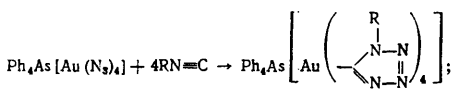
Bistetra-azotriarylphosphine complexes of copper, palladium, platinum, and ruthenium (LXXVI) have been obtained [75,131,138,141,147]† by the interaction of metal azides with nitriles:



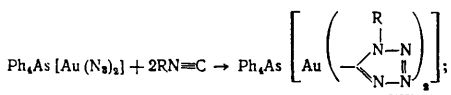
(LXXVI)

The 1,3-DCA involving azidotriphenylphosphinoisonitrile complex on platinum, leading to Pt–N-derivatives of tetrazoles, proceeds analogously.[141]

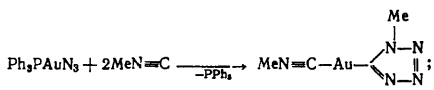
The azide-containing complexes $Ph_4As[Au(N_3)_4]$, $Ph_4As.[Au(N_3)_2]$, $Ph_3PAuN_3$, and $(Ph_3P)_2M(N_3)_2$ (M = Pd, Pt, or Hg) react with isonitriles under very mild conditions, forming tetrazolate complexes[132,140] in which the organometallic substituents are bound to a carbon atom of the tetrazole ring [compounds LXXVII)–LXXXIII)]:



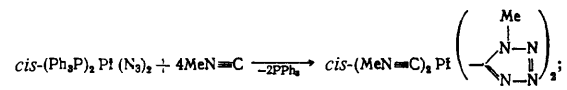
(LXXVII)



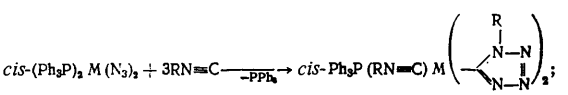
(LXXVIII)



(LXXIX)

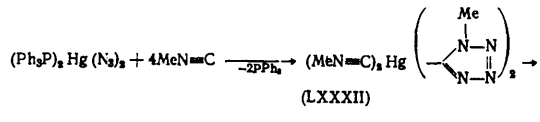


(LXXX)

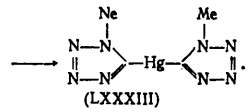


(LXXXI) M=Hg, Pd, Pt

† A whole series of communications[128,144–147] concerning the 1,3-DCA of organoelemental azides to nitriles, isonitriles, and other dipolarophiles, leading to N- and C-substituted tetrazoles, have been published. The examination of all these studies is outside the framework of the present review. In most cases the above investigations were concerned with the reactions of the azides of various metals and provided no fundamental information. We therefore considered the most important and latest studies of this series.



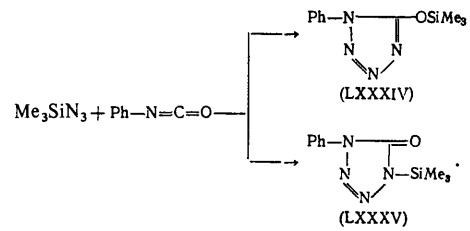
(LXXXII)



(LXXXIII)

Other methods, which are difficult to apply, have been suggested for the synthesis of the complexes (LXXXII)–(LXXXIII).

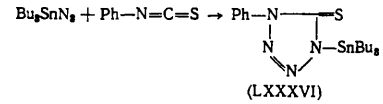
The synthesis of the tetrazolones (LXII, X = O)[128,135] and their thio-analogues (LXII, X = S)[128,131] in accordance with Scheme 2 (pathway *e* usually take place under fairly severe conditions in the presence of catalysts. Thus the 1,3-DCA of trimethylsilyl azide to phenyl isocyanate, which takes place on heating to 140 °C for 12 h in the presence of $AlCl_3$, leads to the silyloxytetrazole (LXXIV) and the *N*-silyltetrazole (LXXXV):[135]



(LXXXIV)

(LXXXV)

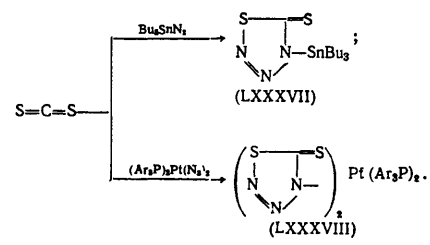
A reaction involving tributylstannyl azide and phenyl isothiocyanate has also been described,[131] although the authors postulate only one structure for the 1,3-DCA product—that of the thionotetrazole (LXXXVI):



(LXXXVI)

The 1,3-DCA reactions of platinum- and palladium-substituted bistriphenylphosphine azides proceed in accordance with analogous mechanisms.[128]

Carbon disulphide has also been used as the heterocumulene dipolarophile:[128,131–133] the 1,3-DCA leads to extremely unusual heterocycles—the thionotriatriazoles (LXXXVII) and (LXXXVIII), the possibility of the synthesis of which by other methods is obscure:[40–43]



(LXXXVII)

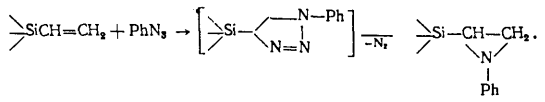
(LXXXVIII)

## 2. The Syntheses of Heterocycles Based on Azides and Organoelemental Dipolarophiles

### *(a) Triazolines and Aziridines*

*C*-Organosilicon derivatives of aziridine have been obtained[148–150] by the interaction of vinylsilanes with phenyl azide at room temperature[149–150] or of alkenylmethylsiloxanes

with benzoyl azide at 60–80 °C.[148] The first stage of this reaction is apparently the addition of the azide to the vinyl group with formation of a five-membered ring, which eliminates a nitrogen molecule and is converted into the *N*-phenylaziridine derivatives (LXXXIX):



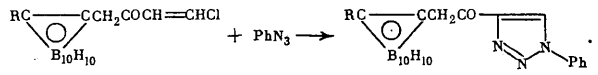
(LXXXIX)

The yields of *C*-aziridinyl derivatives after a 40-day reaction of vinylheptamethylcyclotetrasilane or 3-vinylheptamethyltrisiloxane with phenyl azide did not exceed 11%. The reaction of allylsilanes with $PhN_3$, is even more difficult,[150] while phenyl azide adds somewhat more readily to 3-vinylheptamethyltrisilane;[150] the yield of the reaction product in petroleum ether after ten days at 30–40 °C reaches 40.5%.[148]

When the alkenylsilanes RCH=CHSiR′ are used in the reaction with *p*-bromophenyl azide, 1-*p*-bromophenyl-2-trimethylsilyl-3-R-aziridines are formed.[151] On heating $PhCH{=}CHSiMe_3$ with $p\text{-}BrC_6H_4N_3$ in $CCl_4$ for 24 h, it is possible to isolate 1-*p*-bromophenyl-5-phenyl-4-trimethylsilyl-$\Delta^2$-1,2,3-triazoline in 10% yield. On further heating in the course of 4 days, the triazoline is converted into an aziridine and a 1 : 1 mixture of $Me_3SiCHN_2$ and $PhCH{=}NC_6H_4.Br\text{-}p$.

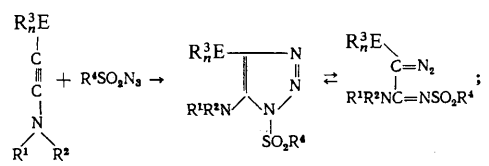
*(b) Triazoles*

4-(*o*-Carbaboranylacetyl)-1-phenyltriazoles (XC) are formed after prolonged heating of carbaboranylmethyl β-chlorovinyl ketone with phenyl azide in benzene solution:[152]



(XC)

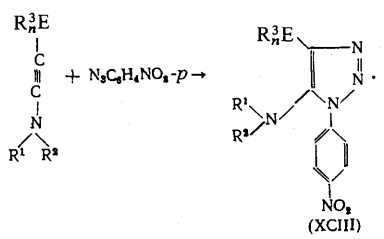
The reactions of sulphonyl azides with organometallic ynamines are regiospecific[153,154] and lead to 5-amino-1,2,3-triazoles (XCI), which, depending on the nature of the substituents $R^1$, $R^2$, $R^3$, and $R^4$, either isomerise wholly to the α-metallated diazoacetamidines (XCII) or are involved in a tautomeric equilibrium with the latter:



(XCI) (XCII)

$R^1$, $R^2$, $R^4$=alkyl, aryl; $R_n^3E = R_2^1As$, $R_2^1Sb$, $R_3^1Si$, $R_3^1Ge$, $R_3^1Sn$, $Ph_2P(O)-$, $Ph_2P(S)-$.

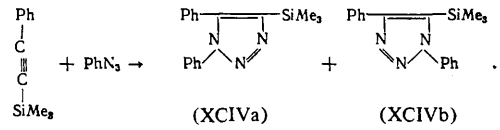
The analogous triazoles (XCIII) with *N*-*p*-nitrophenyl substituents instead of the sulpho-group are more stable:[155]



(XCIII)

We may note that tolyl azide does not react with phenylacetylene itself but does react with its sodium salt.[153] There are also data indicating the condensation of various lithium and magnesium acetylides with azides.[156,157]

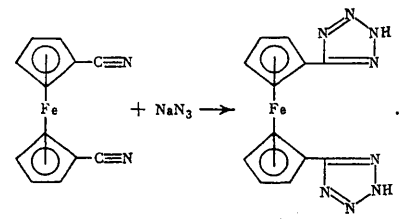
In contrast to the 1,3-DCA with participation of diazoalkanes, which exhibits an appreciable structural specificity in reactions with alkynes, in the case of azides, such specificity is not always marked. However, an appreciable selectivity of the addition reaction, leading to the preferential formation of one isomer, for example (XCIVa), has been sometimes noted; the second isomer (XCIVb) has been obtained in a yield of only 3%:[117,120]



(XCIVa) (XCIVb)

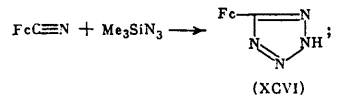
*(c) Tetrazoles*

The interaction of 1,1′-dicyanoferrocene with $NaN_3$ in THF in the presence of $AlCl_3$ leads to the formation of 1,1-di(5-tetrazolyl)ferrocene (XCV):[158]

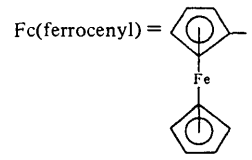


(XCV)

The *C*-ferrocenyltetrazole (XCVI) is formed in the reaction of 1-cyanoferrocene and trimethylsilyl azide in *o*-dichlorobenzene in the presence of $AlCl_3$:[159]



(XCVI)



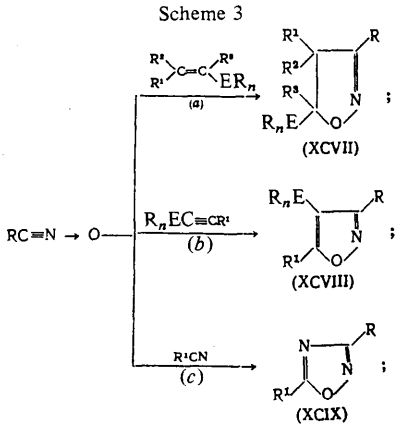
We must emphasise that, so far as we are aware, organoelemental derivatives of heterocumulenes have not been introduced into this type of 1,3-DCA, although the dipolarophiles have been fairly thoroughly investigated (see, for example, Refs.160–162).

## IV. SYNTHESES WITH PARTICIPATION OF NITRILE *N*-OXIDES

1,3-DCA with participation of nitrile *N*-oxides as dipolarophiles, which arise in the course of the reaction and react *in situ*, have been used fairly widely in the synthesis of heterocycles with organoelemental substituents.[95,163–173] The reactions lead to the formation of *NO*-heterocyclic systems—isoxazolines (XCVII), isoxazoles (XCVIII), and oxadiazoles

(XCIX), the methods of synthesis of which are illustrated in Scheme 3:

Scheme 3



(XCVII)

(XCVIII)

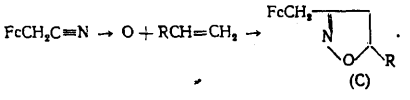
(XCIX)

*a*) and *b*) $R_nE$ = carbaborane- and ferrocene-containing groups, R = Ar, and $R^1$, $R^2$, $R^3$ = alkyl or aryl; *c*) R = $FcCH_2$ and R = Me.

## 1. The Syntheses of Heterocycles from Organoelemental Nitrile *N*-oxides

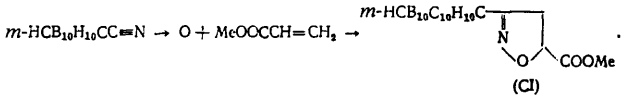
### *(a) Isoxazolines*

Ferrocenylacetonitrile *N*-oxide, formed from ferrocenylnitroethane, reacts *in situ* with a series of olefinic dipolarophiles—hept-1-ene, styrene, acrylonitrile, or trimethylsilylethylene, forming isoxazolines (C):[163]



(C)

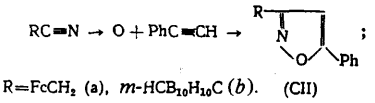
*m*-Carbaboranylnitrile *N*-oxide has been synthesised.[164] Its reaction *in situ* with methyl acrylate leads to an isoxazoline having a *m*-carbaboranyl substituent (CI):



(CI)

### *(b) Isoxazoles*

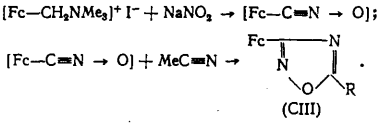
The interaction of phenylacetylene with ferrocenylacetonitrile *N*-oxide or with *m*-carbaboranylnitrile *N*-oxide, obtained *in situ*, results in the formation of the corresponding isoxazoles (CII):[163,164]



R=$FcCH_2$ (a), *m*-$HCB_{10}H_{10}C$ (*b*). (CII)

### *(c) Oxadiazoles*

The reaction of ferrocenylmethyltrimethylammonium iodide with sodium nitrite and acetonitrile, which entails the formation of ferrocenyloxadiazole (CIII),[165] probably involves a stage in which ferrocenylacetonitrile *N*-oxide is formed *in situ*:

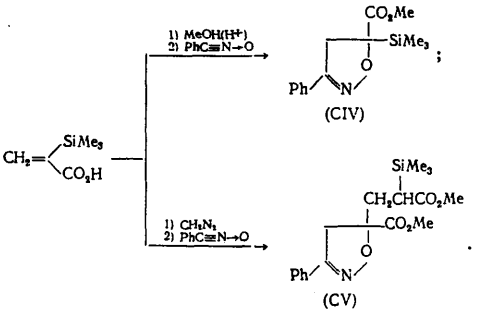


(CIII)

## 2. The Synthesis of Heterocycles from Nitrile *N*-oxides and Organoelemental Dipolarophiles

### *(a) Isoxazolines*

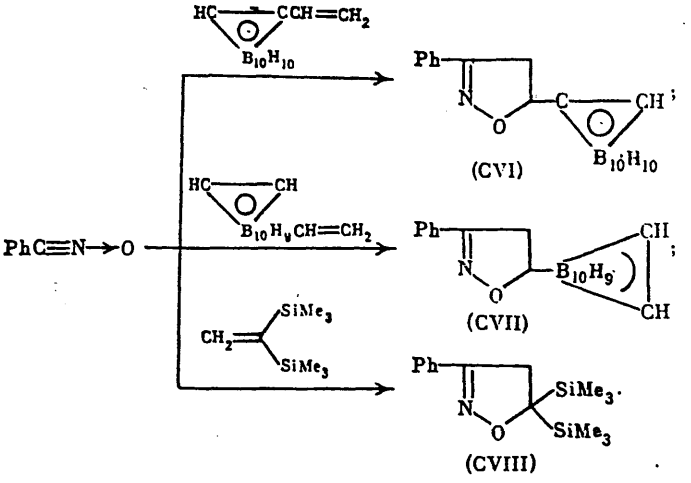
Isoxazolines (XCVII) are formed in the course of 1,3-DCA of nitrile *N*-oxides to dipolarophiles containing a double bond (Scheme 3, pathway *a*). Thus treatment of benzonitrile with methyl α-trimethylsilylacrylate affords the isoisoxazoline (CIV). The interaction of 2-trimethylsilylacrylic acid with benzonitrile oxide leads mainly to the product (CV):[95,166]



(CIV)

(CV)

The 1,3-DCA of benzonitrile oxide to unsaturated *o*-carbaborane derivatives gives rise to the isoxazolines (CVI) and (CVII) with a *o*-carboboranyl substituent, while the interaction of 1,1-bis(trimethylsilyl)ethylene results in the formation of the disilylated isoxazoline (CVIII):[164,166]



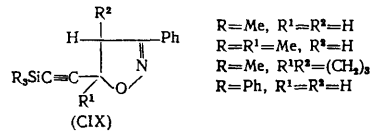
(CVI)

(CVII)

(CVIII)

The study of the competitive reactions of benzonitrile *N*-oxide with dipolarophiles containing double and triple bonds established that the 1,3-DCA is exclusive to the new reaction centre and leads to isoxazolines with silylethynyl substituents.[167,168] Thus the interaction of 1,3-enyne silylhydrocarbons (1-trimethylsilylbut-3-en-1-yne, 1-trimethylsilyl-3-methylbut-3-en-1-yne, 1-trimethylsilylethynylcyclopentene, and 1-triphenylsilylbut-3-en-1-yne) with

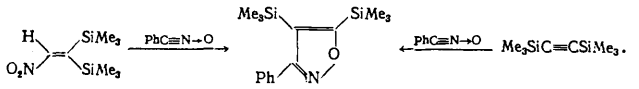
benzonitrile oxide results in the formation of compound (CIX) in satisfactory yields:[168]



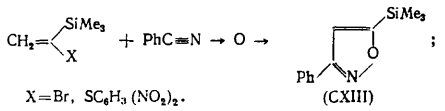
(CIX)

*(b) Isoxazoles*

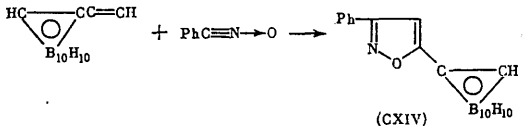
Disilylated isoxazoles of the type of compound (CXI) are obtained instead of the expected isoxazolines (Scheme 3, pathway *a*) in the interaction of nitrovinylidenebistrimethylsilane (CX) with benzonitrile oxide.[95,166] There is in general no doubt about the structure of the isoxazole (CXI), since it has been obtained by specific synthesis from bis(trimethylsilylacetylene). The isoxazole (CXI) had been obtained earlier from benzonitrile oxide and bis(trimethylsilyl)acetylene:[169]


(CX) (CXI) (CXII)

The isoxazole (CXIII) is formed analogously instead of isoxazolines on interaction of α-bromovinyltrimethylsilane or α-(2,4-dinitriphenylthio)vinyltrimethylsilane with benzonitrile oxide:[166]

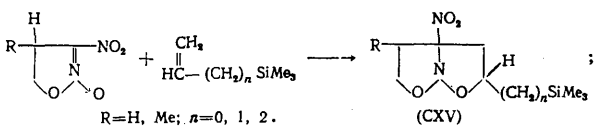

X=Br, $SC_6H_3(NO_2)_2$. (CXIII)

The 1,3-DCA of 1-ethynyl-*o*-carbaborane to benzonitrile oxide leads to the formation, as was to be expected, of the *o*-carbaboranylisoxazole (CXIV):[164]


(CXIV)

*(c) Isoxazolidines*

3-Nitroisoxazoline *N*-oxides react with silylolefins to form the bicyclic isoxazolidines (CXV):[170]

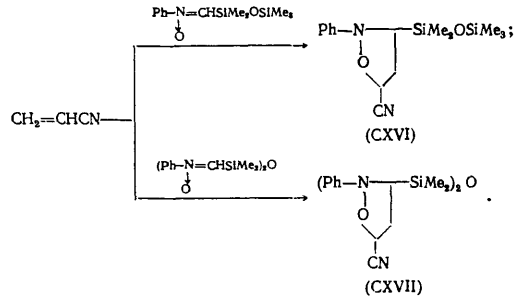

R=H, Me; *n*=0, 1, 2. (CXV)

## V. SYNTHESES WITH PARTICIPATION OF NITRONES

### 1. The Synthesis of Heterocycles from Organoelemental Nitrones

*(a) Isoxazolidines*

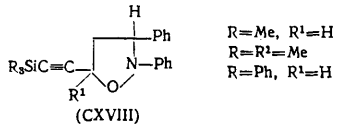
The 1,3-DCA of organosilicon nitrones to compounds containing a double bond results in the formation of derivatives of fully saturated *NO*-heterocycles—isoxazolidines. However, these 1,3-dipoles exhibit a weak affinity for olefins—the cycloaddition products (CXVI) and (CXVII) are obtained in low yields only after the reactants have been allowed to stand for a long time:[171]


(CXVI) (CXVII)

### 2. The Synthesis of Heterocycles from Nitrones and Organoelemental Dipolarophiles

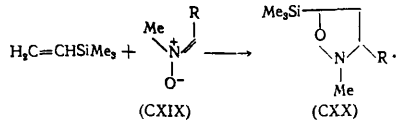
*(a) Isoxazolidines*

The addition of α*N*-diphenylnitrone to silylethynylalkenes (1-trimethylsilylbut-3-en-1-yne, 1-trimethylsilyl-3-methylbut-3-en-1-yne, and 1-triphenylsilylbut-3-en-1-yne) takes place at the double bond with formation of 5-organylsilylethynyl-2,3-diphenyloxazolidines (CXVIII):[168]

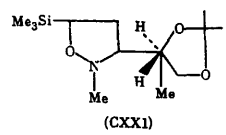


(CXVIII)

The reaction of trimethylvinylsilane with the nitrone (CXIX) affords 5-trimethylsilylisoxazolidine (CXX):[172,173]


(CXIX) (CXX)

The demonstration of the possibility of this reaction enabled the authors[173] to employ the principle in the synthesis of two stereoisomeric isoxazolidines (CXXI) which are deoxysugar derivatives:


(CXXI)

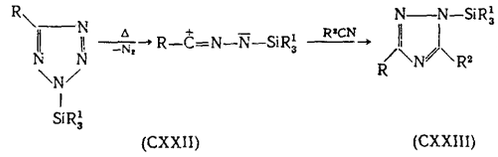
## VI. SYNTHESES WITH PARTICIPATION OF NITRILE IMINES

Nitrile imines are 1,3-dipoles which react exclusively *in situ*. Their 1,3-DCA reactions lead to the formation of pyrazolines (in reactions with olefins)[168,174] or 1,3,4-triazoles (in reactions with nitriles as dipolarophiles).[114]

### 1. The Synthesis of Heterocycles from Organoelemental Nitrile Imines

#### *(a) Triazoles*

Silylated nitrile imines (CXXII) are formed when *N*-silyltetrazoles are heated, the 1,3-DCA to the nitrile resulting in the formation of 2-trimethylsilyl-1,2,4-triazoles (CXXIII):[114]

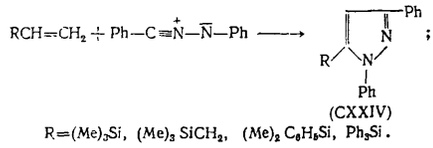


(CXXII) (CXXIII)

### 2. The Synthesis of Heterocycles from Nitrile Imines and Organoelemental Dipolarophiles

#### *(a) Pyrazolines*

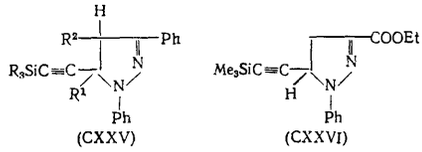
The reactions of dimethylvinylsilane, trimethylvinylsilane, and triphenylvinylsilane with diphenylnitrile imine give satisfactory yields of derivatives of 1,3-diphenyl-2-pyrazoline with organosilicon substituents in the 5-position of the heterocycle as in compound (CXXIV).[174] The dipolarophile activity of the double bond in allyltrimethylsilane is much lower and the 2-pyrazolines are formed in lower yields:



(CXXIV)

R=$(Me)_3Si$, $(Me)_3SiCH_2$, $(Me)_2C_6H_5Si$, $Ph_3Si$.

2,3-Enyne silylhydrocarbons (1-trimethylsilylbut-3-en-1-yne, 1-trimethylsilyl-3-methylbut-3-en-1-yne, 1-trimethylsilylethynylcyclopentene, and 1-triphenylsilylbut-3-en-1-yne) also react with diphenyl nitrile imine as the double bond with formation of 2-pyrazolidines (CXXV).[168] *C*-ethoxycarbonyl-*N*-phenylnitrile imine adds to 1-trimethylsilylbut-3-en-1-yne to form 3-ethoxycarbonyl-1-phenyl-5-trimethylsilylethynyl-2-pyrazoline (CXXVI):[168]



(CXXV) (CXXVI)

## VII. CONCLUSION

The data presented in this review clearly indicate the extensive possibilities for the use of 1,3-DCA in the synthesis of heterocycles with organoelemental substituents. This aspect is important for the chemistry of heterocyclic compounds, since it enables one to avoid the use of complete heterocycles, whose preparation frequently involves multistage syntheses or the application of initial reactants which are difficult to obtain.[40-43]

This review was devoted to 1,3-DCA, but it is already clear[42,66] that other types of cycloaddition used to construct heterocyclic systems can also be regarded as universal methods of synthesis of heterocycles with organoelemental substituents: "2 + 1 = 3", "2 + 2 = 4", and "4 + 2 = 6" additions in the syntheses of three-membered, four-membered, and six-membered heterocycles. Examples of such reactions are available in the literature for organoelemental reagents. Thus the [2 + 2]-cycloaddition of heterocumulenes to a cobalt complex led to the synthesis of metallocyclic compounds.[175,176]

The [2 + 2]-cycloaddition of triphenylstibazosulphonylarenes to diethyl acetylenedicarboxylate gives rise to a four-membered stiba-azaheterocycle.[177]

In addition, one should bear in mind that five-membered heterocyclic systems with organoelemental substituents can be obtained, by analogy with the data quoted by Paquette,[42] Grimmett,[44] and Grüning and Lorberth,[178] as a result of [4 + 1]-cycloaddition, while condensed heterocycles can be produced by intramolecular 1,3-cycloaddition.[66]

In connection with the above, it appears useful to modify both 1,3-dipoles and dipolarophiles by introducing organoelemental substituents and also to employ other types of cycloaddition in order to extend the number of types of heterocycles with organoelemental fragments. The development of new methods of synthesis of organoelemental dipoles and dipolarophiles is also useful in this connection (see, for example, Refs. 179–186).

In our view, the study of the physicochemical properties, structure, and reactivity of heterocycles with organoelemental substituents may be of considerable interest; this field of the chemistry of heterocyclic and organoelemental compounds has been little studied and this is why some of the data presented above concerning the structures of heterocycles with organoelemental substituents are open to doubt. In particular, such heterocycles with organometallic substituents contain simultaneously electron-donating (the N, O, and S heteroatoms) and electron-accepting (M = Ge, Sn, Pb, etc.) centres. Most of them should therefore[1,2] have oligomeric or polymeric structures. This question so far remains open, since in the studies examined above the molecular weights of the heterocycles synthesised were frequently not measured and no mass-spectrometric investigations were made. In this connection, we may note that the dimers (L) described in a series of studies,[107-111] especially the dimers of germylpyrazoles, can also have a different structure (with involvement of the Ge and N atoms of the pyrazole ring), which is extremely characteristic of boron, aluminium, and other organoelemental derivatives of azoles.[1,2,6]

The extensive possibilities for the synthesis of heterocycles with organoelemental substituents with the aid of 1,3-DCA and other types of cycloaddition and the investigation of the nature of this process can be considered also in terms of another aspect, associated with the study of the mechanisms of the reactions of organometallic compounds,[187] including also a wide variety of different types of elementotropic processes.[7-13] The influence of the nature of elements entering into the composition of the fragments of 1,3-dipoles and dipolarophiles considered in this review on the 1,3-DCA mechanism therefore appears to have been inadequately investigated.[61,65,188,189]

Finally, both for a deeper investigation of 1,3-DCA and from the standpoint of the synthesis of heterocycles incorporating different elements in the ring, the study of

the corresponding silyl[190–196] and other organoelemental reagents[175–177,197–201] is of interest. Definite advances in this little investigated field have been made. The first examples of the synthesis of heterocycles by 1,3-DCA with participation of a dipolarophile having a silicon atom in the reaction centre has been described,[190] namely the reaction of 1,1-dimethyl-2,2-bis(trimethylsilyl)-1-silaethylene and trimethylsilyl azide. However, the formation of a silatriazole ring requires more rigorous proof, as has been done in the synthesis of cobalt-containing[175] and arsenic-containing[177] heterocycles.

After the synthesis of silylenes,[191–196] it was natural to attempt to introduce them as dipolarophiles into the 1,3-DCA reaction (see, for example, Masuune et al.).[194] However, it was shown that the cycloaddition product formed in this reaction is unstable; disilacyclopropane was formed as a result.[194]

We believe that the aspects indicated above are promising and can assist in the progess of both theoretical chemistry and the chemistry of heterocyclic and organoelemental compounds.

We emphasise that monographs thematically related to the present review have been published recently.[202,203] However, the aspects of the 1,3-DCA as a general method of synthesis of heterocyclic compounds which we examined are not adequately dealt with in these publications.

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# Catalytic Properties of Hydrogenases

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The review considers the most general physicochemical properties of hydrogenases, the structure of their active centres, and the characteristics of the catalytic reactions in which they participate. It has been suggested that the hydrogenases be divided into one- and many-centre types in terms of the content of the iron-sulphur clusters in the protein molecule. The hydrogenases in these groups differ in their activity and physical and kinetic properties. Much attention has been devoted to the kinetic characteristics of hydrogenases, a scheme for the catalytic reaction has been deduced, and hypotheses have been put forward about the molecular mechanism of the action of these enzymes.
The bibliography includes 145 references.

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## I. INTRODUCTION

Processes involving the absorption and formation of molecular hydrogen in biological systems proceed as a rule with participation of a specific class of enzymes for which the trivial name "hydrogenases" has been proposed.[1] The general scientific and practical interest in these enzymes has been stimulated by a number of their features. Firstly, detailed study of the mechanism of the activation of hydrogen by biological catalysts makes possible a significant progress in our understanding of the physicochemical principles governing the enzyme catalysis of oxidation-reduction reactions as a whole. Secondly, the understanding of the mechanism of these enzymes should greatly facilitate the search for catalysts of the hydrogenation–dehydrogenation reactions of organic compounds which have found extensive practical applications. Furthermore, direct practical use of hydrogenases in reactions involving the oxidation or formation of hydrogen is of great interest. Thirdly, hydrogenases are terminal enzymes in the formation of hydrogen by micro-organisms,[2-4] which can be used, in particular for the utilisation of solar energy for the industrial preparation of hydrogen (the biophotolysis of water).[5] Furthermore, there is a possibility of creating model biochemical systems which effect the photodecomposition of water into hydrogen and oxygen.[6] Fourthly, the possibility of using enzymes in systems for the bioconversion of energy is extremely promising. The bioelectrocatalysis by hydrogenases can serve as the basis for the creation of fuel electrodes in electrochemical converters (biofuel cells).[7-11]

Hydrogenases are fairly common enzymes, which ensure the energy supply for many organisms by the oxidation of hydrogen. The metabolic pathways in micro-organisms exhibiting hydrogenase activity as well as the location and the functions of the hydrogenases themselves have now been thoroughly investigated. There are also numerous data on the biochemistry of these enzymes.[12-15] However, no general views about the catalytic properties of hydrogenases can be found in the literature and the kinetic characteristics of the individual enzymes are dealt with extremely incompletely and in a contradictory manner.

The aim of the present review is to give a systematic account of data on the catalytic functions of hydrogenases. The authors did not attempt to include all the available literature information about enzymes of this class and their aim was to seek the most general features.

## II. CERTAIN PHYSICOCHEMICAL PROPERTIES OF IRON–SULPHUR PROTEINS

### 1. Hydrogenases as Iron–Sulphur Proteins

The first hypotheses concerning the presence of iron in the active centres of hydrogenases were based on the dependence of the activities of the enzymes on the concentration of iron in the culture medium of the micro-organism.[16] The direct radiochemical determination of the iron content in the fractions exhibiting hydrogenase activity at different stages of the purification of the preparation confirmed the presence of iron in the hydrogenases.[17] In addition, all the investigators, starting from 1943,[18] noted the influence of iron complexones on the activity of hydrogenases. Finally, direct determination by atomic-absorption spectroscopy demonstrated that the active centres of hydrogenases contain non-haem iron.[15]

At the same time a large series of studies devoted to the inhibitor analysis of hydrogenases with the aid of specific reagents for SH groups have been successful. It was established in the 1960's that *p*-chloromercuribenzoate, iodoacetamide, and mersalyl suppress hydrogenase activity.[19,20] However, the latter can be restored by incubation with reducing agents.[20-22] It has been shown[23] that, when the hydrogenase from *Clostridium pasterianum* is inhibited by mersalyl, the mercury ions interact with sulphur atoms, leading to the removal of iron from the active centre. The presence of the so-called "acid-labile" sulphur, which is evolved in the form of hydrogen sulphide on strong acidification of the preparations, has been established independently.[24-26]

At the beginning of the 1970's the presence of 12 iron atoms and 12 acid-labile sulphur atoms in the active centre of the enzyme was observed in a study of the hydrogenase from *Cl. pasterianum*.[24] Subsequent investigations confirmed that iron and sulphur are present in hydrogenases in equimolar amounts. The investigation of the optical spectra of hydrogenases made it possible to discover a chromophoric group, corresponding to an iron–sulphur cluster, in the active centre. The development of quantitative extrusion methods[27] made it possible to establish the identity of the structures of the clusters in the active centres of hydrogenases and low-molecular-weight iron–sulphur proteins. The structure and properties of the latter have been studied much more fully compared with hydrogenases. The characteristic features of the behaviour of the iron–sulphur clusters, which are extremely important for the analysis of the catalytic properties of hydrogenases, can be conveniently considered in relation to ferredoxins.

## 2. The Structure of the Active Centre and the Oxidation–Reduction Properties of Low-Molecular-Weight Iron–Sulphur Proteins

Vigorous study of iron–sulphur proteins began in 1962 when the ferredoxin from *Cl. pasterianum* was discovered.[28] One of the distinctive properties of the metalloproteins of this class is the presence of non-haem iron in the active centre.[29,30] Ferredoxins have a relatively low molecular weight (6000–30000).[29] They differ mainly in the structure of the active centre. The 1Fe proteins of rubredoxins contain one iron atom bound to four sulphur atoms in amino-acid cysteine residues. Apart from the two iron atoms, the 2Fe–2S ferredoxins contain two atoms of acid labile sulphur. The class of 4Fe–4S proteins is of greatest interest. It incorporates both ferredoxins and high potential iron proteins or HIPIP differing in the potentials of oxidation–reduction transitions. The proteins of the 8Fe–8S class and more complex ones do not have independent structures, their active centre being formed from the 2Fe–2S and 4Fe–4S clusters.

The iron–sulphur proteins have come to be divided into two groups in terms of the oxidation-reduction potential. The class incorporating the 2Fe–2S and 4Fe–4S proteins, whose potentials are negative (−0.3–−0.4 V), is largest. Here and henceforth the potential is quoted relative to the normal hydrogen electrode. The 4Fe–4S proteins with potentials of about +0.3 V belong exclusively to the group of high-potential proteins. In order to explain the above difference, the hypothesis of "three states" has been put forward,[31] according to which the transitions in ferredoxins and HIPIP take place between different electronic states of the clusters determined by the ratio of the $Fe^{2+}$ and $Fe^{3+}$ atoms. The discovery of superoxidised ferredoxins ($Fd_{S-ox}$) and super-reduced HIPIP ($HP_{S-red}$) suggested the model of "three states" and the final scheme for the oxidation-reduction transitions in the 4Fe–4S proteins:[32]

$$\begin{array}{ccccc} 4Fe^{2+} & Fe^{3+}+3Fe & 2Fe^{3+}+2Fe^{2+} & 3Fe^{3+}+Fe^{2+} & \\ [Fe_4S]^0 & \leftrightarrow [Fe_4S_4]^{1+} & \leftrightarrow [Fe_4S_4]^{2+} & \leftrightarrow [Fe_4S_4]^{3+} & \\ & Fd_{red} & Fd_{ox} & Fd_{s-ox} & \\ & HP_{s-red} & HP_{red} & HP_{ox} & . \end{array}$$

Here and henceforth the charge on the cluster corresponds to the sum of the charges on the iron and acid–labile sulphur atoms.

The study of the physical properties also led to the elucidation of the nature of the ferredoxin transition in the 2Fe–2S proteins. It was established that in the oxidised cluster both iron atoms are in the +3 oxidation state; the reduction of the cluster leads to the transition of one of the atoms to a bivalent state.[33]

The fact that the iron–sulphur cluster constitutes a single electronic structure is remarkable. Numerous investigations have shown that the iron atoms within the cluster are indistinguishable.[30] In order to account for this effect, the hypothesis of the "antiferromagnetic interaction", based on the valence bond method, has been put forward.[33]

Many investigators (for example, Sweeney and Rabinowitz[34]) have pointed out that the spectroscopic characteristics of the 2Fe–2S and 4Fe–4S clusters are extremely similar and sometimes it is impossible to identify the type of cluster. This is caused by the binding of other chromophores and frequently by the influence of the polypeptide chain itself. These difficulties can be overcome by applying the magnetic circular dichroism method[35] and the effect of the linear electric field, which alters the EPR spectrum.[36] However, the simplest method consists in the study of the EPR spectra in 80% dimethyl sulphoxide at different temperatures.[37]

The number of iron atoms in the active centres of hydrogenases is a multiple of four. The application of the quantitative extrusion method to the 12Fe hydrogenases from *Cl. pasterianum*[27] and *Desulfovibrio vulgaris*[38] demonstrated the presence of only the 4Fe–4S clusters in the active centre. In addition there exists a whole series of enzymes containing one 4Fe–4S cluster per protein molecule. However, two 2Fe–2S clusters were detected together with two 4Fe–4S clusters in a study of the EPR spectra of the 12Fe hydrogenases from *Alcaligenes eutrophus* H16.[39,40] Such detailed studies have not been made for other multicluster hydrogenases, but the presence of the 4Fe–4S cluster in the active centre of the enzyme is apparently always essential for hydrogen catalysis. We shall consider briefly the properties of such clusters.

## 3. The Physical Properties of the 4Fe–4S clusters in Low-Molecular-Weight Proteins

(a) *Optical Properties.* The absorption spectra in the visible region of the iron–sulphur proteins containing clusters in the same oxidation states are identical. The absorption at 400 nm diminishes in the sequence

$$[Fe_4S_4]^{3+} > [Fe_4S_4]^{2+} > [Fe_4S_4]^{1+}.$$

The ratio of the absorptions at 400 and 280 nm is a measure of the ratio of the chromophore and the peptide and is usually employed as an indicator of the purity of the iron–sulphur protein.[34]

(b) *Magnetic Properties.* An even number of unpaired electrons in the cluster predetermines the absence of EPR signals. Thus the $[Fe_4S_4]^{2+}$ state is undetectable by EPR.

The $[Fe_4S_4]^{+}$ clusters have a characteristic EPR spectrum which depends relatively weakly on the polypeptide environment. An axial or orthorhombic signal is observed and the $g$-factor is about 1.96. If one excludes the influence of the peptide by recording the spectrum in 80% dimethyl sulphoxide (DMSO),[27] one can obtain an axial signal with the parameters $g_\perp = 1.94$ and $g_\parallel = 2.05$. Ferredoxins

containing two and more iron–sulphur clusters in the $[Fe_4S_4]^+$ state give rise to a more complex EPR signal, which can be accounted for by spin–spin coupling.[34]

The EPR spectra of the $[Fe_4S_4]^{3+}$ clusters are much more sensitive to the polypeptide environment. They are characterised by the factor $g > 2$ (one unpaired electron per four iron atoms).

(c) *The influence of the protein globule.* The protein globule can have a twofold effect on the properties of the cluster. Firstly, it influences on the choice of the optimum oxidation-reduction transitions (ferredoxins and HIPIP). Secondly, depending on the protein, a fairly wide variation of the oxidation-reduction potential is possible for the same reaction. It has been noted[34] that the potentials of the ferredoxin transition $[Fe_4S_4]^{2+} \leftrightarrow [Fe_4S_4]^+$ vary within the limits of 650 mV, while those of the HIPIP transition $[Fe_4S_4]^{3+} \leftrightarrow [Fe_4S_4]^{2+}$ vary up to 750 mV. The conformational changes of the ferredoxin from *C. acidiurici* in the course of the reduction have been recorded.[41] Carter et al. observed in their study of the high-potential proteins from *Chromatium sp.* by X-ray diffraction[42] that the symmetry of the iron–sulphur cluster changes in the oxidation-reduction transition. The protein globule can stabilise or destabilise a particular state of the cluster by its conformational influence, by acting upon the choice of the optimum transition, on the one hand, and by shifting the thermodynamic equilibrium of the oxidation-reduction reaction and hence its potential, on the other.

It has also been stated in the literature that two 4Fe + 4S clusters, greatly differing in the potential of the same electronic transition $[Fe_4S_4]^{3+} \leftrightarrow [Fe_4S_4]^{2+}$ may be present in the iron–sulphur proteins. Ferredoxin I from *Azotobacter vinelandii*[43] has potentials of −420 and +320 mV, the corresponding potentials of ferredoxin IV from *Rhodospirillium rubrum*[44] are respectively −380 and +355 mV, and those of ferredoxin I from *Myobacterium flavum*[45] are −420 and +230 mV.

The ability of the iron–sulphur protein to be degraded by atmospheric oxygen can be accounted for mainly by the lability of the cluster. It has been shown[46] that the interaction of the 4Fe–4S cluster with $O_2$ leads to the transfer of one iron atom to the solution. The discovery of clusters of the type 3Fe–*n*S confirms this conclusion.

### 4. The 3Fe–*n*S Clusters

The 3Fe–*n*S cluster was first detected in ferredoxin II from *Desulfovibrio gigas*.[47] Then it was shown that the ferredoxin from *Cl. pasterianum* is also converted into a form containing a similar cluster on oxidation with hexacyanoferrate(III).[48]

On reconstructing ferredoxin II from *D. gigas* containing initially one each of the 4Fe–4S and 3Fe–*n*S clusters,[49] it was found that an excess of bivalent iron and $S^{2-}$ leads to the formation of clusters of the first type exclusively. An increase of ionic strength or a decrease of the iron concentration in solution has the same effect involving the appearance of a considerable proportion of the 3Fe–*n*S cluster. Furthermore, there is a possibility of the direct interconversion 4Fe–4S ↔ 3Fe–*n*S.[49] Under severe oxidation conditions [in the presence of hexacyanoferrate(III) and oxygen] the 4Fe–4S clusters are converted into the 3Fe–*n*S form, liberating one bivalent iron atom to the solution. It was found possible to carry out also the reverse process under oxidative conditions, the 3Fe–*n*S clusters are capable of being converted into 4Fe–4S under the influence of dithiothreitol and iron salts.

## III. PHYSICOCHEMICAL PROPERTIES OF HYDROGENASES

### 1. Oxidation-reduction Properties

Hydrogenases are capable of both activating molecular hydrogen and of catalysing its evolution. Numerous experiments designed to isolate and store enzymes under various conditions have shown that, under the influence of atmospheric oxygen, the hydrogenase is converted into an inactive form, which, however, may be reactivated by incubation with reductants. It is of interest to determine the influence of the oxidation-reduction state of the enzyme on its activity.

However, serious errors have been made in some studies of this phenomenon. In the course of the measurement of the activity of the hydrogenase on the basis of the rate of evolution of $H_2$, a number of workers[50–53] determined in essence the potential dependence of the hydrogen electrode (see, for example, Damaskin and Petrii[54]), i.e. the potential of the equilibrium evolution of hydrogen from water. Nevertheless, the loss of activity of the enzyme at potentials less than −480 mV under strongly reductive conditions has been reliably established.[51]

The oxidation-reduction titration of the hydrogenase from *Thiocapsa roseopersicina* using various electron donors made it possible to determine the activation potential ($E = -276 \pm 8$ mV).[55]

Although reduction promotes the activation of hydrogenases, nevertheless the direct reduction of the active centre also leads to the loss of activity. There is no doubt about the inhibiting effect of reducing agents, especially sodium dithionite, on the activity of hydrogenases.[13] Together with the irreversible loss of activity,[56] many investigators point out either a weak effect or the possibility of reactivation[20,55,57,58]). The inactivation of the hydrogenase from *Cl. pasterianum* at potentials below −480 mV was noted above.[51] At low concentrations, sodium dithionite does not affect the rate of evolution of hydrogen which takes place with participation of the enzyme from *D. vulgaris*;[59] an increase of the concentration of the reductant leads to a fall of the activity of the hydrogenase to zero.

Together with the usual "two-sided" hydrogenases, there exist a number of hydrogenases capable mainly of absorbing hydrogen. They are all located in the cells of microorganisms together with nitrogenase, which is apparently a factor determining their physiological function. The activity of the "one-sided" hydrogenases as regards the evolution of hydrogen is usually lower by two orders of magnitude than the activity measured on the basis of the absorption of $H_2$ under the same conditions. The rate of evolution for *Rhodopseudomonas capsulata*,[60] *Cl. pasterianum*,[52] and *Rhizobium japonicum*[61] is 1–3% of the rate of absorption of $H_2$; the corresponding activities of the "one-sided" hydrogenase from *Azotobacter chroococcum*[62] differ by a factor of 200.

It has been suggested[63] that the reduction of "one-sided" hydrogenases takes place even in the positive range of potentials relative to the hydrogen electrode in the same solution. Thus, under conditions thermodynamically favourable for the evolution of hydrogen, the hydrogenase becomes inactive. The inactivating reduction potential for the enzyme from *Rh. capsulata*[63] at pH 7.0 was found to be 340 mV. This quantity depends on the pH: $\partial E/\partial \mathrm{pH} \approx -30$ mV. At pH 5.0 the rates of evolution and absorption of hydrogen are approximately the same.

## 2. Optical Properties

Hydrogenases have optical spectra characteristic of iron–sulphur proteins. An absorption maximum at a wavelength of approximately 400 nm is observed in the visible region. The extinction coefficients of hydrogenases calculated per iron atom are usually 4000 litre $mol^{-1}$ $cm^{-1}$, but may deviate significantly from this value.[14,15] When hydrogenases are reduced to the active state by various agents (including sodium dithionite and hydrogen), the absorption at 400 nm diminishes by 10–20%.[14]

## 3. EPR Spectra

Hydrogenases give rise to EPR signals characteristic of iron–sulhpur proteins. In terms of the character of the changes in the EPR spectra during the oxidation–reduction of the active centre, hydrogenases can be divided into two groups. The one-centre enzymes, i.e. those containing one 4Fe–4S cluster, have in the oxidised state an EPR spectrum with $g > 2$, which is extremely similar to the spectrum of the high-potential proteins in the oxidised state, i.e. the spectrum of the $[Fe_4S_4]^{3+}$ cluster. When these hydrogenases are reduced, the EPR signal vanishes. Consequently the oxidation-reduction transition in the enzymes of this group corresponds to the transformation $[Fe_4S_4]^{3+} \leftrightarrow [Fe_4S_4]^{2+}$. Such data have been obtained for the hydrogenases from *Th. roseopersicina* and *Rh. capsulata*,[63] *Rhodospirillium rubrum*,[64,66] *Chromatium vinosum*,[67] and *Chromatium sp.*[68] The authors of the last investigation noted, like Zorin et al,[63] that carbon monoxide does not affect the EPR signals of hydrogenases either in the oxidised or reduced states.

Many-centre hydrogenases (containing more than four iron atoms in the active centre) behave in a significantly different manner. Whereas in the oxidised state they too give rise to EPR signals resembling the $[Fe_4S_4]^{3+}$ signal, after reduction, spectra characteristic of reduced ferredoxins are observed, i.e. characteristic of the state of the $[Fe_4S_4]^{+}$ cluster with the typical $g = 1.94$. The hydrogenase from *Megasphaera elsdenii*, containing three clusters per molecule, has an EPR signal with $g > 2$ in the oxidised state, which is somewhat atypical for HIPIP; when it is reduced, the characteristic ferredoxin spectrum is manifested.[69] Conversely, the hydrogenase from *Cl. pasterianum*, containing 12 iron atoms in the centre, is characterised in the reduced state by the presence of an additional "extraordinary" signal in the ferredoxin spectrum.[70] The authors believe that in the oxidised state only the $[Fe_4S_4]^{3+}$ signal is observed. The number of 4Fe–4S clusters in the hydrogenase from *D. vulgaris* is three.[38,71,72] The EPR spectra of this hydrogenase are typical for many-centre hydrogenases.[38,73]

The oxidation-reduction titration of the enzyme from *A. eutrophus* H16, containing 12 iron atoms per molecule, at different temperatures in 80% DMSO made it possible to distinguish the EPR signals of the two 4Fe–4S and two 2Fe–2S centres.[39,40] The electronic transitions take place at potentials of −445 and −325 mV respectively.

Thus the one-centre hydrogenases in the oxidised state contain the $[Fe_4S_4]^{3+}$ cluster. On reduction, they pass to an active state corresponding to the $[Fe_4S_4]^{2+}$ form. The oxidation-reduction potentials of the above electronic transitions lie mainly in the negative region (for example, at −276 mV for *Th. roseopersicina*[55]). Consequently, the hydrogenases of this type have the properties of low-potential HIPIP proteins. Re-reduction leads apparently to a transition to the $[Fe_4S_4]^{+}$ state in which the enzymes are inactive.

The situation is more complex for many-centre hydrogenases. In the reduced state the EPR spectra resemble those of the $[Fe_4S_4]^{+}$ clusters, while in the oxidised state they resemble the spectra of $[Fe_4S_4]^{3+}$. Chen suggested that in the hydrogenase from *Cl. pasterianum*,[52] containing three 4Fe–4S centres,[27] there are two $[Fe_4S_4]^{2+}$ clusters and one $[Fe_4S_4]^{+}$ cluster in the oxidised state and two $[Fe_4S_4]^{+}$ clusters and one $[Fe_4S_4]^{2+}$ cluster in the reduced state. However, the simultaneous transfer of three electrons (in the potential range 50–60 mV) is possible only for vigorously isolated clusters, while the available data indicate the interaction of the latter. It has been shown[38] that the three-centre hydrogenase (incorporating three clusters of the 4Fe–4S type) from *D. vulgaris* contains no $[Fe_4S_4]^{3+}$ clusters in the oxidised state. The form of the spectrum of this hydrogenase, resembling the HIPIP spectrum, is apparently due to the spin–spin coupling of the clusters in other oxidation states, namely $[Fe_4S_4]^{2+}$ and $[Fe_4S_4]^{+}$. Unfortunately, it was not possible to determine the electronic structure of the active centre of the hydrogenase in greater detail.

## 4. The Relation between the Physical and Catalytic Properties of Hydrogenases

It is of interest to compare not only the physical but also the catalytic properties of the one-centre and many-centre hydrogenases. The Table shows that the activity of the latter, as regards the absorption and evolution of hydrogen, is on average higher by two orders of magnitude than that of the one-centre enzymes. It will be shown below that the cleavage of the hydrogen molecule and the proton exchange with the solvent are not rate-limiting in the $H_2$ activation and evolution reactions.

On this basis, one can put forward two hypotheses concerning the role of the iron–sulphur clusters in catalysis. According to the first, the cluster is an electronic structure stabilising the transition state and hence reducing the height of the activation barrier (see, for example, Berezin and Martinek[77]). The hydrogen oxidation pathway via the intermediate formation of the charged forms of the enzyme ($E^-$ and $E^{2-}$), of the kind suggested, for example, by Chen[52] is unlikely. On the other hand, the undue stabilisation of the intermediate complex leads to an increase of the height of the activation barrier.[77]

According to the second hypothesis, the change in the symmetry of the iron–sulphur clusters in oxidation–reduction transitions (see above) can entail an enforced stabilisation or destabilisation of one of the electronic states under the influence of the thermal movement of the protein globule, which decreases the activation energy via the entropy term.

However, the presence of iron–sulphur clusters in the protein molecule is insufficient for the manifestation of the hydrogenase activity. In contrast to one-centre hydrogenases, the low-potential HIPIP catalyse neither the evolution nor the absorption of hydrogen. An example has been provided by the ferredoxins from *D. gigas*[78] and *M. flavum*,[45] containing four iron atoms per molecule and having oxidation-reduction potentials of −130 and −420 mV respectively, as well as the 6Fe ferredoxins from *T. thermophilis*,[79] whose potential is −250 mV.

## 5. The Role of Nickel in the Hydrogenase Catalysis

The studies in recent years have shown that the presence of nickel in the active centre is extremely important for the manifestation of the hydrogenase activity. This conclusion originated from experiments concerning the effect of the nickel content of the culture medium on the synthesis of hydrogenases during the growth of the micro-organism. It has been shown[80] that the addition of EDTA (at a concentration of 150 μM) to the propagation media of three different cultures (*Azospirillium brasilense*, *A.lipoberum*, and *Derxia gummosa*) suppresses the synthesis of the hydrogenase without influencing significantly the activity and only the introduction of catalytic amounts of bivalent nickel ions (10 μM) makes it possible to abolish the inhibiting effect of EDTA. A correlation has been found[81] between the absorption of radioactive $^{63}Ni^{2+}$ by the cells of *Azotobacter chroococcum* and their hydrogenase activity. The addition of bivalent nickel ions to the culture medium of *Chromatium vinosum*[82] increases the activity of the hydrogenase by a factor of 3–6 without affecting the rate of growth of the micro-organism.

It has been observed that, during the purification of the hydrogenase from *Vibrio succinogenes*,[83] nickel is washed out of the preparation. The authors state that the dependence of the activity of the enzyme on the $Ni^{2+}$ concentration is represented by a straight line passing through the origin of coordinates. Admittedly, individual points on this straight line corresponded to specimens of the enzymes with different degrees of purity.

The involvement of nickel in the hydrogenase catalysis has been confirmed by physicochemical data. The EPR spectrum of the enzyme from *Chromatium vinosum*[82,84,85] shows that the 4Fe–4S cluster interacts with the nickel centre. The effect of the latter is not manifested in a hydrogen atmosphere. The unperturbed spectrum of the cluster can be observed when it is converted into the 3Fe–*n*S form, which, as stated by the authors, is catalytically inactive. Nickel has also been detected by EPR in the hydrogenases from *M.thermoautotrophicum*,[86] *D.gigas*,[87] and *D.vulgaris*.[38]

The EPR spectra of the nickel present in the hydrogenase from *D.gigas* have been studied for different oxidation-reduction states of the enzyme.[87–89] It has been shown that the nickel centre is capable of entering into a one-electron exchange reaction, altering the oxidation state. The potential of this transition is −220 mV at pH 8.5 [88] and depends greatly on the pH ($\partial E/\partial pH = -60$ mV).[89] Thus the reaction is proton-dependent, the $Ni^{3+}$ form being singly protonated:

$$Ni^{3+}+H^{+}+\bar{e}\rightleftharpoons Ni^{2+}H^{+} \qquad (1)$$

Bearing in mind the character of the oxidation-reduction transition (1), we normalise the potentials at pH 7.0. Very close values are obtained for the many-centre enzyme from *D.gigas*[88,89] and the one-centre enzyme from *Chromatium vinosum*[85] (−140 and −150 mV respectively). In the active state of the hydrogenase (in the vicinity of the hydrogen electrode potential) the nickel exists in a bivalent state.

It has been suggested[85] that the nickel centre is the primary acceptor of the hydrogen molecule. It is believed that the Ni atom has an octahedral environment with five occupied coordination centres and one centre capable of being substituted. According to EPR data the minimum distance between the iron and nickel atoms in the hydrogenase from *Chromatium vinosum* does not exceed 12 Å.

Comparative characteristics of the physical and catalytic properties of certain hydrogenases.

| Source of hydrogenase | Content per molecule | | Molecular weight | Type of EPR spectra | | Activity, μmol $H_2$ $min^{-1}$ $mg^{-1}$ | | Substrate | Refs. |
|---|---|---|---|---|---|---|---|---|---|
| | Fe | S | | oxidised state | reduced state | absorption of $H_2$ | evolution of $H_2$ | | |
| *Th. roseopersicina* | 4 | 4 | 68 000 (1×47 000, 1×25 000)* | HIPIP | — | 1.2<br>19.0 | 5.0<br>— | MV<br>BV | [55] |
| *Rh. capsulata* | 4 | 4 | 73 000 | HIPIP | — | 0.075<br>0.83<br>1.1 | 0.012<br>—<br>— | MV<br>BV<br>MC | [74,75] |
| *Rh. rubrum* | 4 | 4 | 67 000 | HIPIP | — | 0.26<br>1.8<br>2.5 | 26.0<br>7.0 | MV<br>BV<br>MC | [64,65] |
| *Chromatium vinosum* | 4 | 4 | 61 000–63 000 | HIPIP | — | — | 425 | MV | [67] |
| *Chromatium sp.* | 4 | 4 | 98 000 (2×50 000)* | HIPIP | — | 210<br>78<br>— | —<br>—<br>39 | MC<br>BV<br>MV | [22]<br>[68] |
| *Megasphaera elsdenii* | 12 | 12 | 50 000 | HIPIP (atypical) | —<br>$g$=1.94 | —<br>— | 630<br>8400** | MV | [69,71,76] |
| *Cl. pasterianum* | 12 | 12 | 60 000 | HIPIP | Fd spectrum; $g\cong 2.0$ | 1660<br>—<br>— | 317<br>3960<br>4000**<br>5000** | MV<br>MV+Fd<br>MV<br>MV+Fd | [24]<br>[52] |
| *D. vulgaris* | 12 | 12 | 50 000 | $g\cong 2.0$ | $g_{\perp}$=1.86<br>$g_{\parallel}$=2.03 | 4600**<br>5000**<br>—<br>— | —<br>—<br>3800<br>10 400** | MV<br>BV<br>MV | [72]<br>[71] |

Notation: MV = methylviologen; BV = benzylviologen; MB = Methylene Blue.

*The subunit composition is given in brackets.
**The maximum reaction rates are quoted.

### 6. Characteristics of the Catalysis by the Hydrogenase from *A. eutrophus*

The hydrogenase from *A. eutrophus* includes yet another group involved in hydrogen catalysis, namely the flavin mononucleotide (FMN),[57] which is responsible for its NADH-dehydrogenase activity. The enzyme molecule (molecular weight 180000–200000) contains 12 atoms of iron and acid-labile sulphur each, combined in two 4Fe–4S and two 2Fe-2S clusters,[39,40] and two FMN molecules.[90] The enzyme consists of four subunits, the hydrogenase activity being manifested solely by the complete molecule,[91] while the NADH-dehydrogenase activity is retained in subunits with molecular weights up to 60000. The enzyme from *A. eutrophus* has unique properties, behaving simultaneously as a hydrogenase and a NADH-dehydrogenase. During the oxidation of hydrogen, the electron density acceptor (via intermolecular electron transfer), is FMN which is capable of reacting subsequently with NAD, reducing it to NADH. It has been shown[92] that methylviologen is able to "intercept" the electron density on the way to the FMN molecule. We may note that the reduced FMN is weakly oxidised by oxygen, like NADH. As a result, NAD should react with FMNH even under aerobic conditions. Indeed, the rate of reduction of NAD by hydrogen, catalysed by the hydrogenase from *A. eutrophus* Z1, is virtually the same in an open cuvette and under anaerobic conditions.[93] The competitive inhibition of the enzyme from *A. eutrophus* H16 [94] by oxygen with respect to $H_2$ has been noted. In the subsequent stages the electron density remains inaccessible to $O_2$. Thus the unique characteristic of the hydrogenase of *A. eutrophus* consists in the fact that this enzyme is capable of oxidising hydrogen with subsequent reduction of the acceptor, which has a low negative potential, almost independently of the presence of oxygen. This is so far impossible on any other catalyst.

## IV. THE INFLUENCE OF VARIOUS EFFECTS ON THE ACTIVITY OF HYDROGENASES

### 1. The Role of the Ionic Strength of the Solution

Contradictory data concerning the influence of the ionic strength of the solution on the activity of hydrogenases have been quoted in the literature. For example, a high ionic strength has an inhibiting effect on the enzymes from *Paracoccus denitrificans*[95,96] and *D. vulgaris*.[71] The activity of the hydrogenase from *Chromatium vinosum*[67] falls appreciably in the presence of cobalt sulphate and chloride. The enzymes from *Chromatium sp.*[22] are inhibited by heavy metal ions.

On the other hand, the activity of the hydrogenase from *Megasphaera elsdenii*[69,71] increases with increase of the ionic strength of the solution. The stabilising effect of chlorides at concentrations in excess of 0.7 M on the enzyme from *Rh. rubrum* has been noted.[97] The hydrogenase from *Spirilina maxima*[98] is inactivated by copper and zinc ions, but the presence of iron, manganese, magnesium, and calcium leads to a slight activation.

The contradictory nature of the above data gives some indication of the mechanism of the effects. The ionic strength apparently acts on the protein globule. Evidently the proteins of even a single micro-organism, located in different places within the cell, can show significant differences. In conclusion, we may mention the retention of the activity of the hydrogenase from *D. vulgaris*[99] in the lyophilised state.

### 2. The Effect of Iron Complexones

At the beginning of the 1970's many workers observed a strong inhibition of the activity of hydrogenases by iron complexones: αα′-bipyridyl, *o*-phenanthroline, EDTA, $CN^-$, and $N_3^-$ (see, for example, Bone[20] and Hashke and Campbell[100]). However, it was found subsequently that the above reagents have only a weak effect on the activity of the enzymes from *Chromatium sp.*[22] and *D. vulgaris*.[101] The hydrogenases from *Anabaena cylindrica*[102] and *E. coli*[103] are not inhibited by αα′-bipyridyl, while the enzyme from *Chromatium vinosum*[67] is unaffected by $CN^-$ and $N_3^-$. Furthermore, EDTA, αα′-bipyridyl, and *o*-phenanthroline have a prolonged effect against the inactivation of the hydrogenase from *Cl. pasterianum* by oxygen,[104] while $CN^-$, $N_3^-$, and $F^-$ do not affect its activity at concentrations up to $10^{-2}$ M.[105]

Although it has been recognised that the above iron complexones are not inhibitors of hydrogenases,[14,15] studies are still being published in which a decrease of their activity in the presence of EDTA, $CN^-$, and $N_3^-$ has been noted.[98] The effect of these reagents is apparently associated with the partial degradation of the iron–sulphur cluster and should therefore depend on the stability of the latter. Indeed, the stability of the hydrogenase from *A. cylindrica* with respect to inactivation by oxygen has been noted in a study[102] where the absence of an effect by αα′-bipyridyl on the activity of the enzyme was observed. The unusual stability of the clusters from *Chromatium sp.* with respect to extrusion[106] agrees well with their insensitivity to iron complexones.[22]

The effect of carbon monoxide should be considered specially. The inhibiting action of CO has been found in all studies in which its influence on the activity of hydrogenases has been investigated. It is difficult to suppose that this entails any changes in the electronic structure of the iron–sulphur cluster, because CO shows no effect on its EPR spectrum.[67,68] It has been established that one CO molecule is adsorbed on the active centre of the enzyme.[67,102] In the hydrogen oxidation reaction the inhibition by carbon monoxide is competitive with respect to $H_2$ [105,107–109] and non-competitive with respect to the electron acceptor.[107,108] Thus, within the framework of the hypothesis that the nickel centre is an acceptor of the $H_2$ molecule while the iron–sulphur cluster stabilises the intermediate state in electron transfer, the inhibiting effect of CO can be readily accounted for. Carbon monoxide evidently blocks the free coordination site in the nickel centre which is inaccessible to larger complexones. The hydrogen molecule is also adsorbed at this coordination site.

### 3. The Mechanisms of the Inactivation of Hydrogenases by Oxygen

The high sensitivity of hydrogenases to oxygen is well known. Attempts have therefore been sometimes made to extract the enzymes from strict anaerobes under the conditions of the controlled absence of $O_2$.[24,100,110] Subsequent studies led to the abandonment of this complication in biological techniques. Two mechanisms for the action of oxygen on the activity of hydrogenases have been discovered: (1) reversible oxidation of the active centre in which the possibility of its reactivation by a reductant remains; (2) slow irreversible inactivation. The occurrence of the latter has been demonstrated.[111]

The slow irreversible inactivation in air is characteristic of all hydrogenases. Nevertheless the enzymes of *A.eutrophus* Z1 proved to be more stable on storage in air than in an atmosphere of a pure inert gas or hydrogen.[93] The stabilising effect of oxidants has also been noted in other studies.[39,40] The kinetics of the irreversible inactivation of hydrogenases by oxygen indicate a distinct two-phase character of the process,[93,112,114] the reduced form of the enzyme being labile and the oxidised form stable.[93] The conclusion that the oxidised hydrogenase is more resistant to $O_2$ than the reduced form has been confirmed also by other data.[39,71,113]

The attempts to stabilise hydrogenases in air are associated in the first place with immobilisation. The two-phase character of the inactivation of the enzyme from *Cl.pasterianum*[114] persisted also after immobilisation on glass, but its stabilisation was then achieved. The degree of blocking of the active centre of the enzyme, determined from the ratio of its activity in the presence of low-molecular-weight (methylviologen) and high-molecular-weight (ferredoxin) electron transferring agents, is satisfactorily correlated with the stabilising effect.

A novel method for protecting against $O_2$ has been proposed.[115] By immobilising the protein on the charged surface of a polyanionic adsorbent, it is possible to create a microenvironment in which "gasses are salted out". The adsorption of the hydrogenase from *Cl.pasterianum* on DEAE-cellulose or Dowex 1-X2 increased the stability of the enzyme in air by a factor of 20–25. It was noted that at a low ionic strength hydrogen was also no longer in contact with the hydrogenase. Consequently, when this method is used, the reaction can be effected only in the direction of $H_2$ evolution.

However, another stabilisation procedure, which throws light on the mechanism of the inactivating effect of oxygen, is the most interesting. It has been found that iron complexones (EDTA, αα′-bipyridyl, *o*-phenanthroline, and Chelex-100) at concentrations in the range 0.01–0.5 M have a prolonged effect on the hydrogenase from *Cl.pasterianum*,[104] while αα′-bipyridyl and benzylviologen[103] lower the rate of the oxygen inactivation of the enzyme from *E.coli*. Finally, the protecting effect of carbon monoxide against the action of $O_2$ has been observed and it has been shown that the hydrogenase from *Chlamydomonas reinhardi* reacts with one oxygen molecule at the rate-limiting stage of the inactivation process.[116]

It has been reported that the reduction of the reduced enzyme from *A.eutrophus* H16 with $O_2$ leads to the appearance in solution of the superoxide radical-ions $O_2^{\cdot-}$.[117] Like hydrogen peroxide, the latter inactivate the hydrogenases from *E.coli*, *Cl.pasterianum*,[103] *Th.roseopersicina*, and *Rh.capsulata*[118] more strongly than does molecular oxygen. It may be that this is one of the factors determining the relative lability of the reduced forms of the enzymes. However, the superoxide radical-ions had no effect on the hydrogenase from *A.eutrophus H*16.[94]

The degradation of the iron–sulphur clusters in hydrogenases by oxygen is to some extent analogous to the interconversion in ferredoxins. The 4Fe–4S cluster is capable of being converted into the 3Fe–*n*S form with liberation of an iron atom into the solution, especially under the influence of $O_2$.[49] The 3Fe–*n*S cluster is believed to be inactive in hydrogen catalysis.[82,84,85,87] Furthermore, in studies[84,85] of the EPR spectra of the hydrogenase from *Chromatium vinosum* it was found that the interconversion interferes with the electronic interaction of the iron–sulphur and nickel centres, which is also important for catalysis. It has been suggested that the iron atom nearest to nickel is liberated from the cluster. However, the attempts to reconstruct the hydrogenases by analogy with ferredoxins[49] led to the recovery of only traces of activity for *D.vulgaris*[119] and were unsuccessful in many instances. However, there exists an indirect confirmation of the proposed hypothesis. The fact that bivalent iron ions stabilise the hydrogenase from *Azotobacter chroococcum* and prevent the loss of its activity[62] can be interpreted as a consequence of their effect on the kinetics of the degradation of the 4Fe–4S cluster, which takes place with the evolution of a bivalent ion into the solution.

Another consequence of the effect of oxygen on hydrogenases is rapid reversible inhibition. As already stated, the enzymes isolated and stored in air are in an inactive state. They can be reactivated by adding reducing agents. Furthermore, in the oxidation of $H_2$ or in deuterium exchange there is a possibility of an autocatalytic acceleration of the reaction after an induction period.[20,57,120–122]

The phenomenon of autocatalysis has been studied in detail in relation to the enzymes from *Th.roseopersicina*[120] and *A.eutrophus*.[93] It was shown that the induction period decreases or is completely eliminated after the addition of reducing agents, for example sodium dithionite, or very small amounts of the product, i.e. the reduced form of the electron acceptor. The lag period is shortened also after increasing the concentrations of the enzyme[93,120,122,123] and the electron acceptor,[120] which is extremely characteristic of reactions under autocatalytic conditions.[120] However, the opposite variation has been observed in the reduction of NAD by hydrogen, which is catalysed by the hydrogenase from *A.eutrophus* Z1: the induction period increases with increase of the NAD concentration.[93] We may recall that NADH inhibits the hydrogenase from *A.eutrophus* Z1 [91] by cleaving it into subunits. The superposition of the inhibition by the product does in fact lead to this type of extraordinary variation.

The question of the mechanism of the activation of hydrogenases is of fundamental importance: does it occur under the influence of hydrogen, in the reduced electron acceptor, or as a result of a proenzyme–enzyme interaction. Data on autocatalysis have shown that there is no direct activation of the enzyme by hydrogen. In the oxidation of hydrogen by methylviologen,[120] the hydrogenase from *Th.roseopersicina* is activated solely by the interaction of the inactive enzyme with the reduced methylviologen. However, one should note that the concentration of $MV^{2+}$ in this reaction was much higher than in the enzyme concentration.

The study of the deuterium exchange involving the hydrogenase from *A.eutrophus H*16 [123] showed that in solution the enzyme can be activated also in the absence of an electron transferring agent, while in the immobilised state the free electron transferring agent is essential for this purpose in the absence of the enzyme–enzyme interaction. The impossibility of activating the enzyme directly by hydrogen has also been confirmed in another study.[92] Consequently the activity of the hydrogenase irreversibly inactivated by oxygen can be restored under autocatalytic conditions via the interaction either with the reduced form of the electron transferring agent or with the molecules of the active enzyme.

The "oxygenation" hypothesis was proposed in 1954, according to which[122] the reversible inactivating effect of oxygen reduces to the formation of a complex and not to an oxidation-reduction reaction:

$$E + O_2 \rightleftarrows EO_2,$$

where $EO_2$ and E are the inactive and active forms of the

enzyme. Oxygen can be evolved from the active centre of the enzyme as a result of dissociation. The authors believe[122] that the hydrogenase is activated in this way.

Since this theory has gained fairly wide currency,[13,15] it is essential to consider it in greater detail. The authors[122] believe that the correlation between the "oxygen-absorption" activity of the reductant and the decrease of the induction period for the hydrogenase from *P. vulgaris* constitute proof of "oxygenation". However, the lag period in the oxidation of hydrogen catalysed by the hydrogenase from *A. eutrophus* is eliminated both as a result of the glucose oxidase reaction (glucose + glucose oxidase),[121] which the above authors[122] regard as one of the best "deoxygenants", and after the addition of very small amounts of NADH ($10^{-4}$ M),[93] which interact very weakly with $O_2$. We may note the potential of the oxidation of glucose to gluconate[124] is $-0.42$ V.[7] Oxygen may not be the only oxidant in this reaction. Finally, data for the oxidation-reduction transitions in the active centres of hydrogenases on activation (see above) are entirely inconsistent with the "oxygenation" hypothesis.

Autocatalysis takes place owing to the presence of micro-amounts of the active form of the enzyme, which are inevitably present even at high positive potentials. In the initial stages of the reaction, oxygen is present in solution, so that $O_2$ reacts with the reduced forms of the enzyme and the electron transferring agent. A dependence on the oxygen concentration appears as a result and this has been recorded.[122] The competition between autocatalysis and the inhibition of the reaction by oxygen leads to the appearance, in the general case, of more complex dependences of the rate of acceleration on the specific activity of the hydrogenase, the oxidation-reduction potentials of the enzyme and the electron acceptor, and the concentrations of all the components, including $O_2$. The existence of a threshhold concentration of the enzyme has been indicated.[123]

### 4. The Effect of the pH of the Medium on Catalysis by Hydrogenases

The effect of the concentration of hydrogen ions on the kinetics of reactions with participation of hydrogenases is determined by a large number of factors. Protons are the product of the reaction

$$H_2 \rightleftarrows 2H^+ + 2\bar{e}.$$

Consequently a change in their concentration entails a shift of the thermodynamic equilibrium and it is known that a shift of the equilibrium hydrogen potential per pH unit is 59.2 mV. Thus the activity of electron acceptors in the oxidation of $H_2$ should also depend on the pH. Indeed, the optimum absorption of hydrogen is as a rule attained in the region of alkaline pH, while the optimum evolution occurs in the region of acid pH.[13-15]

However, for certain hydrogenases, for example, those from *Chromatium sp.*,[22] *Th. roseopersicina*,[125] and *Rh. capsulata*,[126] the rate of oxidation of hydrogen by methylviologen in the pH range 7–9 is independent of the proton concentration. The kinetics of the catalysis by hydrogenases will be examined in the next Section.

The proton concentration can influence not only the thermodynamic and kinetic parameters of the reaction itself but also a whole series of other factors. Firstly, one cannot rule out the presence in the protein of ionogenic groups which influence the catalysis. Secondly, the oxidation-reduction transitions in the iron–sulphur clusters and nickel centres also depend on the pH. Thirdly, the proton concentration can influence the properties of the electron transferring and reducing agents. For example, a shift of the pH optimum has been observed[19] in the deuterium exchange reaction catalysed by the hydrogenase from *D. desulfuricans* on activation by various reducing agents.

It is believed that the reduced form of methylviologen is capable of being protonated and decolorised in the range pH < 6.0.[15] Fernandez and co-workers[126] explained the decolorisation of $mV^+$ in acid solutions, observed by other workers, by the loss of the reducing capacity of sodium dithionite, whose oxidation-reduction potential depends on the pH. In the reduction of methylviologen by metallic zinc, the extinction coefficient of the reduced form of the former was independent of the pH up to 5.0.[127]

## V. KINETICS OF THE REACTIONS CATALYSED BY HYDROGENASES

Both in nature and in artificial systems hydrogenases can catalyse reactions of two types. On the one hand, they activate molecular hydrogen for subsequent reactions, including the oxidation of $H_2$. On the other hand, hydrogenases are capable of catalysing the evolution of hydrogen. The deuterium exchange and hydrogen ortho–para conversion reactions include both processes. Overall, these enzymes accelerate the equilibration in the system

$$H_2 \rightleftarrows 2H^+ + 2\bar{e}.$$

The above reactions can be used to measure the hydrogenase activity. The methods involving the evolution of hydrogen should be especially considered. It has been found[128] that, when the reaction mixture is shaken at a frequency greater than 200 cycles per minute, the $H_2$ evolution process is not controlled by diffusion. The above conditions are still used in most investigations. However, judging from the latest data,[63] it is impossible to attain the independence of the rate of evolution of hydrogen of the rate of stirring and of the area of the interface between the liquid and gas phases, i.e. the processes associated with the evolution of $H_2$ are nevertheless complicated by diffusion. The method for the determination of the concentration of hydrogen in solution at the Clark electrode[129] also suffers from a series of disadvantages. Furthermore, the evolution of $H_2$ from the reduced forms of methylviologen and other electron transferring agents can be complicated by the re-reduction of the hydrogenase. We shall therefore concentrate attention on the kinetics of the processes associated with the activation of hydrogen.

### 1. Activation of the Hydrogen Molecule at the Active Centres of Hydrogenases

It has been suggested that the rate-limiting stage of the process is the cleavage of the $H_2$ molecule in the active centres of hydrogenases.[125] However, the order of the reaction involving the oxidation of hydrogen by methylviologen in the presence of hydrogenases from *Th. roseopersicina*[130] and *Rh. capsulata*[126] with respect to $H_2$ is zero. The study of the isotope effects observed when hydrogen is replaced by deuterium in the activation process with participation of the hydrogenases from *A. eutrophus*, *D. desulfuricans*, and *Rh. japonicum*,[92,131,132] confirmed that the cleavage of the $H_2$ molecule is the rate-determining stage in the reaction.

The question of the nature of this cleavage is of fundamental importance for catalysis. There exists the view that the cleavage of hydrogen in the active centres of hydrogenases takes place heterolytically. The view is based, in particular, on a study[133] where only the intermediate HD was detected in the gas phase in the course of an investigation of the hydrogenase-catalysed isotope exchange between $H_2$ and $D_2O$. However, the final exchange product $D_2$ was detected in the same system.[128]

Subsequently it was suggested[22] that the rates of formation of the exchange reaction products HD and $D_2$ be compared. The ratio of the rates $v_{HD}/v_{D_2}$ ($v_{HD}/v_{H_2}$) depends on a whole series of parameters, for example, on the concentration and activity of the enzyme, so that its numerical values cannot serve as a characteristic of the system. Nevertheless, it is noteworthy that, when the exchange reactions with participation of the hydrogenases from *Chromatium sp.*,[22] *D. desulfuricans*,[134] *D. vulgaris*,[128] *Th. roseopersicina*,[135] *A. eutrophus*,[123] and *Rh. japonicum*[132] were carried out, the rates of formation of HD were of the same order of magnitude as the rates of formation of $D_2$ and as a rule were not lower than the latter. According to Gitilitz and Krasna,[22] this must be regarded as undoubted evidence in support of the heterolytic mechanism of the cleavage of the $H_2$ molecule, because at a platinum catalyst the product HD is almost absent, in contrast to $D_2$. However, platinum is a many-centre catalyst, so that each hydrogen atom behaves independently after the dissociation of the molecule, while the active centre of the hydrogenase is an isolated electronic system with rigorously defined oxidation-reduction electronic transitions.

The ratio of the rates of formation of the intermediate and the exchange products falls with increase of the enzyme concentration, which supports, together with the data quoted above, the model

$$H_2 + E \rightleftharpoons EH^- + H^+.$$

It has been found that the ratio $HD/D_2$ is independent of the partial pressure of hydrogen.[128] This finding does not disprove the model (2), because it can be accounted for also within the framework of this scheme, for example, when the orders of the formation reactions of HD and $D_2$ with respect to $H_2$ are the same.

The dependence of the rate of deuterium exchange in the presence of the hydrogenase from *Rh. japonicum*[132] on the pH parallels the influence of the pH on the rate of evolution of hydrogen. On the other hand, the rate of absorption of $H_2$ is relatively independent of the proton concentration within the same limits.

The above results support the mechanism of the activation of hydrogen via the intermediate formation of an enzyme–hydride complex $EH^-$. There are no important facts in the literature in conflict with this mechanism. Furthermore, in a number of studies on the kinetics of reactions with participation of hydrogenases there are direct indications of the possibility that the process occurs via the intermediate formation of $EH^-$.[52,123,128,132]

However, this does not as yet permit conclusions about the mechanism of the activation and cleavage of the hydrogen molecule in the active centres of hydrogenases. It is appropriate to quote at this point the energy cycle for the reaction between $H_2$ and protons[136] (the numerical values are given in kcal $mol^{-1}$):

$$\begin{array}{ccc} H_2 & \xrightarrow{101} & 2H \\ {\scriptstyle 398}\downarrow & & \downarrow{\scriptstyle 2\times 312} \\ H^- + H^+ & \xrightarrow[327]{} & 2H^+ \end{array}.$$

For reactions in an aqueous medium, it is essential to take into account the solvation energy.[137] Thus only 33 kcal $mol^{-1}$ has to be expended on the heterolytic dissociation of the hydrogen molecule in solution.

The active centres of one-centre hydrogenases contain the $[Fe_4S_4]^{2+}$ cluster and $Ni^{2+}$. Nor can one rule out the possibility of the homolytic dissociation of the $H_2$ molecule as a result of the redistribution of the electron density and the formation of a covalent bond. Next, as a result of the rapid intramolecular reaction in the active centre of the hydrogenase, there is a possibility of the liberation of protons and of the formation of the EH form in order to compensate for the energy expenditure.

We shall now proceed to the discussion of the activation of the $H_2$ molecule in the active centres of hydrogenases in the course of its oxidation. We shall consider initially the question of the mutual effect of two substrates: the electron acceptor and $H_2$. As already stated, carbon monoxide is a competitive inhibitor with respect to hydrogen and a non-competitive inhibitor with respect to the electron acceptor. Study of the mutual effect of $H_2$ and the oxidised form of methylviologen showed that, in the case of the hydrogenases from *Cl. pasterianum*,[108,138] *M. thermoautotrophicum*,[109] and *Rh. japonicum*,[107] these substrates react with different sections of the active centres. On the other hand, the electron acceptors whose nature is significantly different, namely the high-molecular-weight cytochrome $c_3$ and the low-molecular-weight methylviologen, interact with the same section of the active centre of the hydrogenase from *D. vulgaris*.[139] Thus the electron acceptor and $H_2$ molecules each add to their own section of the active centres of the hydrogenases in the hydrogen oxidation reaction.

The processes in which hydrogen is activated by hydrogenases are fairly rapid. In the $H_2$ oxidation reaction catalysed by the one-centre enzymes from *Th. roseopersicina*[130] and *Rh. capsulata*,[126] the reaction is of zero order with respect to hydrogen. This finding is fairly unexpected for the kinetics of processes with participation of hydrogenases. The dependence on the hydrogen concentration of the oxidation of $H_2$ by methylviologen had been described earlier for the hydrogenases from *Cl. pasterianum*[108,138] and *D. vulgaris*[140] by the classical Michaelis function. The non-zero reaction order with respect to $H_2$ is manifested also in the oxidation of the latter by Methylene Blue in the presence of the hydrogenase from *Rh. japonicum*.[107]

The difference between the enzymes from *Th. roseopersicina* and *Rh. capsulata*, on the one hand, and the enzymes from *Cl. pasterianum* and *D. vulgaris*, on the other, consists in the fact that the former are one-centre enzymes, while the latter are many-centre hydrogenases (see Table). The physical properties of the enzyme from *Rh. japonicum* have been less thoroughly investigated, but, it has been shown[61] that it contains 12 iron atoms per protein molecule.

The kinetic parameters of the reactions with participation of the hydrogenases in this group depend in different ways on the pH. In the course of the oxidation of hydrogen by methylviologen with participation of the enzyme from *Cl. pasterianum*,[108] the ratio of the maximum rate of reaction to the Michaelis constant ($V_{max}/K_M$) increases with decrease of the concentration of protons in the pH range 8–10. $V_{max}$ does not then change and $K_M$ decreases sharply. This confirms indirectly the conclusion that the oxidised form of methylviologen reacts with the enzyme–hydride complex $EH^-$. Unfortunately, in the remaining cases, it is not possible to discover rigorously the influence of the pH on the reaction kinetics.

In the oxidation of $H_2$ by methylviologen with participation of the one-centre hydrogenases from *Th. roseopersicina*[125] and *Rh. capsulata*[126] in the pH range 7–9, the maximum rate

and the Michaelis constant are independent of the hydrogen ion concentrations. The parameters of the overall kinetic curves remain unchanged when the pH is varied within the same limits.[130]

The fact that the rate of the enzyme reaction can be of zero order with respect to the substrate and the product is misunderstood in the literature. Thus the authors of a review,[15] criticising the results of Varfolomeev et al.,[125] claim from general considerations that the rate of oxidation of hydrogen "must" depend on the pH.

We shall now consider the observed relations taking into account the known rules governing the occurrence of single-pathway catalytic reactions under stationary conditions (see, for example, Karyakin et al.[141]). The concentration of the product does not enter into the rate equations for such reactions if the product formation stage is irreversible. In order to eliminate the influence of the substrate, a further requirement is that its addition should be much faster than the remaining stages of the reaction. Consequently the zero order of the reaction implies that the addition of the hydrogen molecule and the liberation of protons from the active centres of the one-centre hydrogenases from *Th. roseopersicina* and *Rh. capsulata* should be much faster than the remaining stages, including the oxidation-reduction stages.

A detailed study has been made[130] of the kinetics of the oxidation of hydrogen by methylviologen catalysed by the hydrogenase from *Th. roseopersicina*. In order to discover the sequence of the stages, the dependence of $1/V_{max}$ and $K_M/V_{max}$ for both substrates on the pH and the concentration of the second substrate was determined. Kinetic analysis makes it possible to select the unique sequence

$$H_2 \cdot H^+ — MV^{2+} \rightarrow MV^{2+} — H^+ \rightarrow,$$

where the arrow indicates irreversible stages. Thus, according to Karyakin et al.,[130] the electron acceptor reacts with the enzyme–hydride complex $EH^-$; after the elimination of the second acceptor molecule from the active centre, the enzyme remains in the protonated form.

Thus kinetic data confirm the conclusion that the activation of the hydrogen molecule in the active centres of hydrogenases leads to the formation of the enzyme–hydride complex.

The kinetic differences between the many-centre and one-centre hydrogenases can be traced in relation to the enzymes considered. While the kinetic parameters of the hydrogen oxidation reactions in the presence of one-centre hydrogenases are independent of the pH and the $H_2$ concentration, in the presence of many-centre enzymes the reaction can be of zero order with respect to hydrogen and protons. If the rates of the oxidation-reduction stages were comparable for both groups of enzymes, it would follow that the cleavage of the $H_2$ molecule in the presence of many-centre hydrogenases should be slower than in the presence of the one-centre enzymes. However, the opposite behaviour is observed experimentally: the activity of the many-centre hydrogenases is on average higher by two orders of magnitude than that of the one-centre hydrogenases. Thus the rates of the oxidation-reduction stages are much higher for the many-centre hydrogenases than for the one-centre enzymes. This in fact constitutes the main kinetic difference between them.

It would be of interest to compare also the rates of formation of the enzyme–hydride complex for both groups of hydrogenases. However, this would require the knowledge of the dependence of the Michaelis constant (with respect to hydrogen) on the pH. Unfortunately there are no such data in the literature. The hydrogenase from *Th. roseopersicina*[130] forms $EH^-$ at a rate characterised by a constant of the order of $10^5$ $min^{-1}$, which is comparable to the rate constants for reactions catalysed by many-centre hydrogenases (they are calculated from the maximum rates[13,14] see Table), which are of the order of $10^4$–$10^5$ $min^{-1}$. Thus the hydrogen molecule is activated with formation of the enzyme–hydride complex equally fast by both groups of hydrogenases. Since the iron–sulphur clusters of the one-centre and many-centre enzymes have extremely different properties, presumably the hydrogen molecule is not activated at this cluster. This conclusion agrees well with the hypothesis that the nickel centre is the acceptor of the $H_2$ molecule.

The extremely high rate of formation of the enzyme–hydride complex $EH^-$ in the active centres of hydrogenases is noteworthy. The heterolytic dissociation of the $H_2$ molecule under the conditions of the metal complex catalysis[142] is $10^5$–$10^6$ times slower. However, it is as yet not clear what particular mechanism is responsible for such high rates of the enzyme reactions compared with the reactions in the presence of the familiar model catalysts.

## 2. The Oxidation-Reduction Stages

We shall consider the interaction of the enzyme with the electron acceptor in the hydrogen oxidation reaction. Firstly, one should note that a dependence of the catalytic properties of enzymes on numerous factors is characteristic of all enzymes. Thus it has been found that cytochrome $c_3$ appreciably stimulates the activity of the hydrogenase from *D. desulfuricans*.[131] Furthermore, the rate of evolution of hydrogen from the reduced mixture of methylviologen and cytochrome $c_3$ under the influence of this hydrogenase exceeds the sum of the rates of its evolution from methylviologen and the cytochrome taken separately.[139] Inhibitor analysis shows that both acceptors interact with the same section of the active centre in the enzyme.

Secondly, it has been stated by some investigators[108,123] that the deuterium exchange reaction in the active centres of hydrogenases can include oxidation-reduction stages due to the enzyme–enzyme interaction. The addition of an electron acceptor leads to the inhibition of the deuterium exchange with participation of the hydrogenases from *Cl. pasterianum*,[108] *A. eutrophus*,[123] and *Rh. japonicum*.[132] After the complete reduction of the acceptor, the deuterium exchange is renewed. Consequently the pathway associated with the reduction of the electron transferring agent is tentative.

Finally, as established above, the oxidation-reduction stages are rate-limiting in the catalysis of the oxidation of molecular hydrogen by hydrogenases. The dependence of the rate of oxidation of molecular hydrogen catalysed by hydrogenases on the concentration of a one-electron acceptor (methylviologen, benzylviologen) is as a rule described by the Michaelis function. However, in the catalysis by the hydrogenases from *M. elsdenii*[71,76] and *D. vulgaris*[53] the dependence of the reciprocal of the rate of evolution of hydrogen on the reciprocal of the methylviologen concentration is non-linear. This can be accounted for by side effects, for example, by the formation of the dimer of the reduced form of methylviologen,[143] and by the diffusion or re-reduction of the enzyme, because the non-linear dependence of the rate of evolution of hydrogen in terms of the variables of the Lineweaver–Burk equation was found[53,76] to be coupled with a linear dependence of the absorption of hydrogen. Furthermore, it has been discovered[71] that the $H_2$ evolution reaction is of first order with respect to methylviologen for the same hydrogenase from *D. vulgaris* (Hildenborough strain) (cf. Grande et al.[53]).

On the other hand, studies[59,139,140] using the hydrogenase from *D. vulgaris* (Miyazaki strain) led to the discovery of a quadratic dependence of the rates of absorption and evolution of hydrogen on the methylviologen concentration. This contradiction was explained somewhat later.

With rare exceptions, the hydrogen oxidation (and formation) reactions are usually found to be of first order with respect to the electron acceptor. Methylviologen and benzylviologen are one-electron mediators and their interaction with the active centre of the enzyme during the reaction should be separated by an irreversible stage.[130,141]

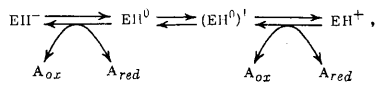
A detailed study has been made[126,130] of the kinetics of the interaction of the enzyme–hydride complex with the electron acceptor. The rate of the hydrogen oxidation reaction is related to the electron acceptor concentration by an expression of the type of the Michaelis equation and the form of the integral curve depends on the concentration of the reduced form of the acceptor. The apparent Michaelis constant is proportional to the concentration of the reduced form of the electron acceptor. Thus the rate equation for the process is

$$v = \frac{V_{max}[S]}{K_M + [S] + K'_p[P]}, \qquad (2)$$

where [S] and [P] are respectively the concentrations of the substrate and the product and $K'_p$ is the product binding constant.

Various possible mechanisms, including the mechanism involving a reversible catalytic stage, the general mechanism with inhibition by the product, and the mechanism with a reversible bimolecular interaction with the substrate have been considered in the course of kinetic analysis. The dependence of the kinetic parameters of Eqn.(3) on the oxidation-reduction potential of the electron acceptor made it possible to give preference to the mechanism with reversible bimolecular interaction:

Scheme 1




where $A_{ox}$ and $A_{red}$ are respectively the oxidised and reduced forms of methylviologen or benzylviologen. Thus a slow intramolecular stage has been discovered in the mechanism of the catalytic reaction.

On the other hand, the $H_2$ oxidation reaction catalysed by the hydrogenase from *Rh. japonicum* is not inhibited by the reduced form of the electron acceptor [Methylene Blue (MB), phenazine metasulphate (PMS)].[107] The oxidation-reduction potentials of the above acceptors are respectively +11 and +80 mV and differ markedly from the potentials of methylviologen and benzylviologen (−440 and −359 mV respectively). Since the "inhibiting" effect is shown to be associated with the reverse reaction, i.e. with the donation of an electron, the behaviour of reduced MB and PMS becomes entirely understandable. Furthermore, Scheme 1 has been derived for a one-electron transferring agent.

In Scheme 1 there is a unimolecular stage between the stages involving interaction with electron acceptors and it is rate-limiting. Its physical significance becomes understandable if account is taken of the fact that the abstraction of the first electron from the hydride ion in the gas phase required approximately twenty times less energy than the abstraction of the second electron. The $\Delta H$ for these processes are respectively 15 and 312 kcal $mol^{-1}$.[136]

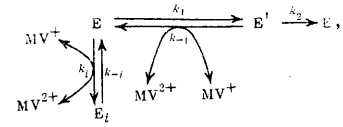
The difference between the many-centre and one-centre hydrogenases may consist both in the different degrees of stabilisation of the intermediate forms and hence in the different ratio of the rates in stages (*1*) and (*3*) in the forward and reverse directions (Scheme 1) and in the acceleration of the intramolecular stage (*2*). As a consequence of this, when the most active hydrogenases are employed, the second order of the reaction with respect to the electron acceptor may be observed. The hydrogenase from *D. vulgaris* (see Table) has established a kind of record as regards activity and the second order of the hydrogen absorption and evolution reactions with respect to methylviologen, observed in the presence of this enzyme, is quite readily explicable.

However, it has been shown[126] that the second order of the reaction with respect to methylviologen is also observed in the hydrogen oxidation reaction in the presence of the hydrogenase from *Rh. capsulata*. This enzyme is a striking representative of the group of one-centre hydrogenases (see Table) and there is therefore no analogy with the hydrogenase from *D. vulgaris*. We may recall that the enzyme from *Rh. capsulata* belongs to the group of "one-centre" hydrogenases:[60,75] The question arises what can be the characteristic features of the enzymes of this group.

A catalyst is incapable of shifting the thermodynamic equilibrium of the reaction. Consequently the only possible explanation is the creation of kinetic hindrance: the acceleration of the forward reaction of the catalyst and its "switching off" along the reverse pathway. It has been suggested[63] that the inactivating re-reduction of one-sided hydrogenases occurs even in the range of positive potentials relative to the hydrogen electrode in the same solution. Thus, under conditions which are thermodynamically favourable for the evolution of hydrogen, the hydrogenase becomes inactive. The inactivating re-reduction potential for the enzyme from *Rh. capsulata*[75] proved to be −340 mV at pH 7.0. The change in potential per pH unit is then approximately −30 mV.

Only the reduced electron acceptor can serve as the electron donor for the re-reduction in the hydrogen oxidation reaction. The simplest scheme of the oxidation-reduction stages in the catalysis by the hydrogenase by *Rh. capsulata* is as follows:

Scheme 2




where $E_i$ is the inactive form of the catalyst.

Using the corresponding rate equation, it is possible to calculate from kinetic data the inactivating re-reduction potential ($E_i \cong -387 \pm 5$ mV at pH 8.5). This value agrees well with that found by oxidation-reduction titration ($E_i \cong -385 \pm 5$ mV).[75] Thus the hypothesis of the inactivating re-reduction as the basis for the regulation of "one-sided" hydrogenases has been confirmed in a direct kinetic study. It must be emphasised that the conclusion that common mechanisms of the catalysis operate has been extended also to the group of "one-sided" enzymes. Their only difference from the two-sided hydrogenases from the kinetic standpoint is the presence of the characteristic inactivating re-reduction stage.

In conclusion we present the final scheme for the catalysis by the hydrogenase from *Th. roseopersicina* (Scheme 2 based on the data of Karyakin and co-workers[126,130]), which is fairly general for hydrogenases from different

sources:

Scheme 3

$$E + H_2 \overset{K_1}{\rightleftarrows} EH_2, \quad (1)$$

$$EH_2 \overset{K_2}{\rightleftarrows} EH^- + H^+, \quad (2)$$

$$EH^- + A_{ox} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} EH^0 + A_{red}, \quad (3)$$

$$EH^0 \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} (EH^0)', \quad (4)$$

$$(EH^0)' + A_{ox} \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} EH^+ + A_{red}, \quad (5)$$

$$EH^+ \underset{K_6}{\rightleftarrows} E + H^+, \quad (6)$$

where E is the hydrogenase and A is methylviologen or benzylviologen. Stages (*1*), (*2*), and (*6*) are of the quasi-equilibrium type. Here the equilibrium is strongly displaced towards the formation of products, so that the occurrence of any kind of irreversibility in the above set of stages is entirely well founded. Stage (*4*) is also irreversible within the framework of the given kinetic conditions. Since the adjoining stages (*3*) and (*5*) can proceed in both forward and reverse directions while stage (*4*) is the slowest, it is reasonable to postulate the simplest type of irreversibility: $[A_{ox}]k_5 \gg k_{-4}$. We may note that the restrictions on the reaction conditions thus obtained involve the concentrations of the reactants. Thus, by changing the process conditions, it is possible to achieve not only reversibility along the sections indicated but also irreversibility in the opposite direction.

## VI. KINETICS OF THE ELECTROCHEMICAL PROCESSES CATALYSED BY HYDROGENASES

The phenomenon of the acceleration of electrode processes by enzymes has been called "bioelectrocatalysis".[7-11] In this case the electrode behaves as one of the reaction substrates, the electron donor, or the electron acceptor. There are two ways of coupling enzyme and electrochemical reactions: the mediator mechanism in which the electron exchange is effected by a transferring agent, capable of reacting both with the electrode and with the active centre of the enzyme, and the direct mechanism in which the enzyme is capable of being directly oxidised or reduced at the electrode.

The mediator bioelectrocatalysis has been achieved using the hydrogenases from *Pr. aestuarii* and *Th. roseopersicina*.[144] It has been shown that the conditions in the oxidation of hydrogen are close to reversibility: depending on the electrode potential, such a system can operate both with absorption and in evolution of hydrogen.

A unique feature of the hydrogenase from *Th. roseopersicina* is its ability to behave as the electrocatalyst of the oxidation-formation of molecular hydrogen in sorption on the surface of a carbon black electrode.[145] It has been shown that, in a $H_2$ atmosphere on an electrode with the immobilised hydrogenase, an equilibrium hydrogen potential is established. In the hydrogen oxidation reaction the current drawn from the electrode is independent of the pH and the partial $H_2$ pressure over the entire overpotential range.[126] The zero order of the electrocatalytic reaction with respect to the substrate and the product permits the conclusion, as in homogeneous reactions, that the addition of a hydrogen molecule and the liberation of protons from the active centre of the enzyme are rapid compared with the oxidation-reduction (in the given instance electrochemical) stages.

The overall polarisation curve for the electrochemical oxidation of $H_2$ is described by the equation corresponding to the occurrence of two consecutive potential-dependent stages involving electron transfer from the active centre of the enzyme to the electrode.[126] It has been shown that the electrochemical stages must follow one after another, i.e. cannot be separated by addition–dissociation processes. The mechanism of the homogeneous reaction includes, in addition, an intramolecular stage separating two oxidation-reduction stages. Evidently in electrocatalysis this stage is concealed in the electrochemical stages; one can only observe that the second electron is transferred to the electrode more slowly than the first.

The parameters of the positive branch of the polarisation curve make it possible to predict the kinetics of the reverse reaction, i.e. of the electroevolution of hydrogen. The negative branch has inferior current characteristics compared with the positive component. Thus the use of the hydrogenase electrode is most justified in the $H_2$ oxidation reaction. Furthermore, the inactivating re-reduction of the active centre of the hydrogenase has been detected in the electrochemical system, which constitutes evidence for the occurrence of this phenomenon, since the possibility of the effect by any other inactivating factors has been ruled out experimentally.

Thus the study of the kinetics of the electrochemical reaction with participation of the hydrogenase from *Th. roseopersicina* not only confirms but also supplements the conclusions concerning the characteristic features of the homogeneous kinetics and the catalytic properties of hydrogenases reached in the previous Section.

## VII. CONCLUSIONS

This review has dealt with the most general physicochemical properties of hydrogenases, the structure of their active centres, and the characteristic features of the catalysis. In conclusion we should like to put forward the hypothesis that the action of these enzymes has a molecular mechanism.

We have been able to divide hydrogenases into two groups differing in their physical properties, activities, and kinetic parameters in the hydrogen oxidation reaction. The one-centre hydrogenases contain one 4Fe–4S cluster. Their activity is on average lower by two orders of magnitude than that of the many-centre hydrogenases containing several iron–sulphur clusters in the active centre. While the addition of a hydrogen molecule and the liberation of protons are effected equally rapidly by both groups of hydrogenases, an appreciable difference is observed in the rates of the oxidation-reduction stages. The latter evidently proceed with participation of the iron–sulphur structures in the active centre.

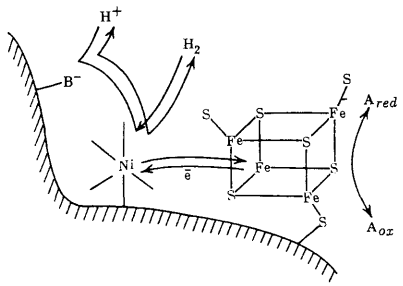
Furthermore, it has been possible to elucidate the kinetic scheme for the hydrogenase catalysis. The activation of the hydrogen molecule in the active centres of hydrogenases leads to the formation of the enzyme–hydride complex $EH^-$. In the $H_2$ oxidation reaction the interaction of the one-electron acceptor with the active centre is a reversible bimolecular process. The addition of the second acceptor molecule is preceded by a slow intramolecular stage.

The involvement of nickel in hydrogenase catalysis is indisputable. This has been confirmed, firstly, by the overlap of the electron orbitals of the nickel and iron–sulphur centres. Secondly, inhibitor analysis and the character of the mutual influence of substrates indicate that the $H_2$ and electron acceptor molecules interact with different sections of the active centre. Furthermore, a parallel has been

traced between the relative equality of the rates of activation of the hydrogen molecule by the one-centre and many-centre hydrogenases and the identity of the oxidation-reduction potentials of their nickel centres, while the properties of the iron–sulphur cluster structures in these two types of hydrogenases differ significantly. Finally, the one-electron reduction of $Ni^{3+}$ to $Ni^{2+}$ requires the participation of a proton acceptor. All these factors support the view that the nickel centre is the initial acceptor of the $H_2$ molecule.

The molecular mechanism of the catalysis by hydrogenases of the hydrogen oxidation reaction can be described with the aid of a two-centre model:

Scheme 3




The $H_2$ molecule is sorbed on a "free" coordination site of nickel, substituting, for example, a water molecule. This is followed by heterolytic dissociation with formation of the enzyme–hydride complex apparently without the involvement of the electron density of the iron–sulphur cluster. The latter is also able to accept one of the electrons of the hydride rapidly and reversibly. The iron–sulphur cluster interacts with the acceptor, giving up the "superfluous" electron, also rapidly and reversibly. The abstraction of the second electron from the hydride ion is known to require the expenditure of more energy by 300 kcal $mol^{-1}$ than the abstraction of the first electron. Consequently, the transfer of the second electron between the nickel and iron–sulphur centres is much slower. This stage is in fact manifested in the kinetics as the slow intramolecular stage. It is also followed by the rapid interaction with the acceptor and by deprotonation. As a result of the superior organisation of the iron–sulphur clusters, many-centre hydrogenases are capable of effecting the intramolecular transfer of the second electron at a higher rate. Overall, the role of the iron–sulphur clusters in hydrogenases consists in the stabilisation of the intermediate electronic states, as in other enzymes, for example, in nitrogenase. The presence of a spatially branched structure is essential for the abolition of the change in the ambient medium when the oxidation state is altered, which leads to a decrease of the activation energy for the electron transfer according to the solvent reorganisation theory.

In the oxidised state, hydrogenases are inactive in the hydrogen oxidation reaction and the possibility of the activation of the $H_2$ molecule is lost. It would appear that the electric field of $Ni^{3+}$ should promote the heterolytic dissociation of the $H_2$ molecule to a greater extent than the $Ni^{2+}$ field. The first step in the activation of the $H_2$ molecule apparently consists in the transfer of an electron to the latter from the active centre of the hydrogenase, which appreciably weakens the H–H bond. The potential of the $Ni^{3+} \leftrightarrow Ni^{2+}$ transition (−150 mV) allows fully the possibility of such donation. If this were followed by the reduction of $Ni^{3+}$ to $Ni^{2+}$, for example, as a result of the reduction of the iron–sulphur cluster $[Fe_4S_4]^{2+}$, then a proton-acceptor group would appear in the coordination sphere of $Ni^{2+}$. Thus the following conditions for the dissociation of the $H_2$ molecule arise in the transition state obtained: (1) the weakening of the H–H bond as a result of the appearance of an electron in the antibonding orbital of the molecule; (2) the presence of a bivalent nickel atom capable of accepting a hydride ion; (3) the appearance of a proton acceptor in the coordination sphere of the nickel centre; (4) the formation of an oxidised iron–sulphur cluster capable of accepting an electron.

As already mentioned, hydrogenases activate the hydrogen molecule and effect the formation of the enzyme–hydride complex at extremely high rates compared with metal complex catalysts. The hydrogenase from *A.eutrophus* is capable of hydrogenating NAD to NADH. Thus specific modification of the active centres of hydrogenases or their modelling leads to a way of creating more effective catalysts of the hydrogenation and dehydrogenation of organic compounds.

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# Geminal Sulphones

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The literature data on the method of synthesis, structures, and chemical properties of compounds containing geminal sulphonyl groups are surveyed and described systematically. The available information about the thermodynamic and kinetic acidities of the compounds and the stability and reactivity of the carbanions stabilised by two (and more) sulphonyl groups is discussed. The bibliography includes 222 references.

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## I. INTRODUCTION

Compounds containing geminal sulphonyl groups were first synthesised at the end of the last century but for a long time their number was small, they were difficult to obtain, and they were inadequately investigated. The first representatives of geminal sulphones (GS) were β-disulphones (DS). Subsequently numerous publications were devoted to the chemistry of DS and at the present time these are the most thoroughly investigated representatives of GS. Studies have developed mainly in two directions during the last three decades on the basis of these compounds: (1) investigation of the thermodynamic and kinetic acidity of GS and the problems of the formation, stabilisation, and reactivity of the corresponding carbanions associated with it; (2) the search for methods of synthesis of various types of GS.

The first direction is represented by studies in which, together with the investigation of the acid properties of GS and of the factors influencing the stabilisation of carbanions and their reactivity (hybridisation of the carbon atom, configuration, conformation, and $2p,3d$-orbital interaction), problems concerning the proton-donating activity of certain representatives of GS in the formation of hydrogen bonds with electron donors were solved.

The second direction developed rapidly in recent years when appreciable advances were achieved in the synthesis of unsaturated GS, in the use of GS for the introduction of sulphonyl groups into heterocyclic compounds, and also in the synthesis of new organophosphorus and organofluorine compounds. It was found that unsaturated GS have specific properties characteristic only of these compounds.

The amount of available information in the literature and the synthesis of properties of GS is sufficient for its survey and systematic treatment. Nevertheless there has so far been no review on the chemistry of GS. Even in the familiar monograph of Oae[1] and the review by Magnus[2] little attention has been devoted to GS.

In the present review the first attempt is made to fill this gap. The data dealt with in the review are described in the following order: we start with the chemistry of β-disulphones and then proceed to unsaturated compounds and more complex structures containing geminal sulphonyl groups.

Information which appeared in the literature during the last forty years, up to July, 1984, has been used in the review. Earlier studies are quoted only when necessary. In considering the theoretical problems concerning the thermodynamic acidity of GS and the stabilisation of the corresponding carbanions, certain aspects of the chemistry of monosulphones are discussed to achieve a fuller description of the problem. Compounds containing geminal sulphonamide groups are not considered in this review.

## II. METHODS OF SYNTHESIS

The methods of preparation of aliphatic GS containing an unsubstituted methylene or methylidyne group reduce to the following fundamental schemes with rare exceptions: (1) synthesis and subsequent oxidation of the geminal bis-sulphides (thioacetals) or tris-sulphides (trithioorthoesters); (2) the introduction of $SO_2R$ groups (or SR groups with subsequent oxidation) in the α-position in compounds containing two geminal electron-accepting groups, one of which is the sulphonyl group. Both methods lead to the formation of methane derivatives. Higher homologues of aliphatic GS are obtained from DS or geminal trisulphones (TS) by alkylation with alkyl halides or via the Michael reaction.

The higher reactivity of the methylene group in DS makes it possible to employ a wide variety of DS for the synthesis of certain unsaturated GS.

### 1. Linear and Cyclic Disulphones

Linear symmetrical GS with a free methylene group (1) were obtained for the first time by condensing formaldehyde[3,4] or its trimer[5,6] with thiophenols or merceptans in the presence of acids with subsequent oxidation of the bis-sulphide formed. These reactions proceed as a rule with satisfactory yields and the availability of the DS is therefore determined by the availability of the corresponding thiol. Methylene chloride[7] or bromide[8] in the presence of alkali metal alkoxides is used much more rarely in the synthesis of bis-sulphides instead of formaldehyde:

$$RSH \xrightarrow[CH_2X_2,\ EtONa]{CH_2O,\ H^+} \xrightarrow{[O]} \underset{(I)}{(RSO_2)_2CH_2}\ ;$$

$$R = Alk, Ar;\ X = Cl, Br\ .$$

A wide variety of oxidants are used in the oxidation stage, among which nitric acid,[9] hydrogen peroxide,[6,10] chromium trioxide,[11,12] peracids,[13] hydroperoxides,[14] and potassium permanganate[15] are most common.

Various aromatic and aliphatic DS have been synthesised by the method which is based on the oxidation-reduction cleavage of arene- or alkane-sulphinylacetic acids obtained from S-substituted mercaptoacetic acid:[16]

$$RSCH_2COOH \xrightarrow[HAc]{H_2O_2} [RSOCH_2COOH] \xrightarrow{H^+} (RS)_2CHCOOH \xrightarrow{H_2O_2} (I)\ ;$$
$$R = Alk, Ar\ .$$

Disulphones with an unsubstituted methylene group (I) have also been synthesised by nucleophilic substitution of halogen atoms in α-halogenosulphones by treating them with alkali metal thiolates and oxidising the resulting sulphone sulphides,[17,18] by chlorinating aryl methyl sulphides with subsequent disproportionation of aryl chloromethyl sulphides on alumina and oxidation of the resulting bis-sulphide,[19] and by oxidising the bis-sulphides formed in the radical reaction of a monochloromethyl ether in the presence of thiols.[20]

Symmetrical DS (II), in which the hydrogen atoms of the methylene group have been substituted by various aliphatic groups, are usually obtained by alkylating unsubstituted DS (see below), although the synthesis by the oxidation of substituted thioacetals and thioketals is also known:[21]

$$RR^1C(SR^2)_2 \rightarrow RR^1C(SO_2R^2)_2\ ;$$
$$(II)$$
$$R, R^1 = Alk;\ R^2 = Alk, Ar\ .$$

A universal method of synthesis of both symmetrical and asymmetric DS has been proposed by Gibson,[22,23] who obtained various DS in high yields by making use of the availability of various alkane- and arene-sulphonyl acetones, the high reactivity of the methylene group in these compounds in thioalkylation and thioarylation reactions, and also the ready heterolytic abstraction of the acetyl group (sometimes even in the oxidation process):

$$RSO_2CH_2COMe \xrightarrow[EtONa]{R^1SX} RSO_2CH(SR^1)COMe \xrightarrow[HAc]{H_2O_2} RSO_2CH_2SO_2R^1\ ;$$
$$R, R^1 = Alk, Ar;\ X = Hal, SO_2Alk, SO_2Ar\ .$$

Substituted DS containing a third electron-accepting substituent at the carbon atom are synthesised by introducing a second sulphonyl group (or SR group with subsequent oxidation) at the methylene carbon atom in compounds of the type $RSO_2CH_2S$. As a rule, the reaction proceeds only with the most reactive sulphonyl chlorides:[24]

$$\left.\begin{array}{l} MeSO_2CH_2CN + PhSO_2Cl \xrightarrow{(>3\%)} \\ PhSO_2CH_2CN + MeSO_2Cl \xrightarrow{(70\%)} \end{array}\right\} \rightarrow PhSO_2CH(CN)SO_2Me\ .$$
$$(III)$$

Owing to the low reactivity of aromatic sulphonyl chlorides, DS substituted by two aromatic groups are synthesised using the corresponding aryl thioesters of sulphinic acid or arenesulphenyl chlorides:[24]

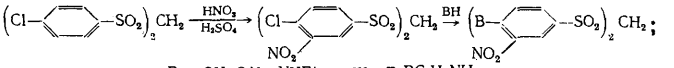
$$PhSO_2CH_2CN \xrightarrow{PSO_2SPh} PhSO_2CH(SPh)CN \xrightarrow{[O]} (PhSO_2)_2CHCN\ .$$
$$(IV)$$

Substituted DS of type (III) substituted by aliphatic and aromatic groups are obtained by employing methanesulphonyl chlorides, which makes it possible to shorten the synthesis by one stage. Asymmetric DS with electron-accepting substituents (CN, COOMe, COOEt, COMe, and COPh) at the methylidyne carbon atom have been synthesised in this way.[25]

Bis(benzenesulphonyl)ethoxycarbonylmethane (V) has been obtained from ethyl dichloroacetate and thiophenol with subsequent oxidation of the reaction product:[26]

$$PhSH + Cl_2CHCOOEt \xrightarrow{EtONa} (PhS)_2CHCOOEt \xrightarrow{[O]} (PhSO_2)_2CHCOOEt\ .$$
$$(V)$$

Nitrodisulphones cannot be obtained by the direct nitration of the methylene group. Nitration of bis(benzenesulphonyl)-methane leads to bis(3-nitrobenzenesulphonyl)methane.[27] Bis(4-chlorobenzenesulphonyl)methane is converted into bis(4-chloro-3-nitrobenzenesulphonyl)methane on nitration.[28] A series of DS containing various substituents in the aromatic ring have been obtained by the nucleophilic substitution of chlorine atoms of the last compound:[28]



$$B = OH, OMe, NHEt, o\text{-}, m\text{-}, p\text{-}RC_6H_4NH.$$

A disulphone with the nitro-group at the methylene carbon atom has been obtained by the alkaline cleavage of tris-(methanesulphonyl)nitromethane:[29]

$$(MeSO_2)_3CNO_2 \xrightarrow{NaOH} (MeSO_2)_2CHNO_2 + MeSO_3Na\ .$$
$$(VI)$$

The synthesis of DS with the $CF_3SO_2$ group has been described.[30] The authors used the usual method for the preparation of the bis-sulphide and oxidised the latter to DS with chromium trioxide in acetic acid:

$$p\text{-}XC_6H_4SNa \xrightarrow{ClCH_2SCF_3} p\text{-}XC_6H_4SCH_2SCF_3 \xrightarrow[HAc]{CrO_3} p\text{-}XC_6H_4SO_2CH_2SO_2CF_3\ ;$$
$$X = H, Cl, NO_2\ .$$

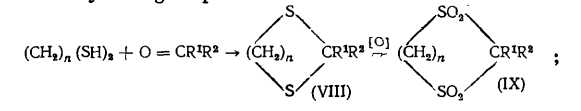
Disulphones with two perfluoroalkyl groups have been obtained from perfluorinated sulphonyl fluoride and Grignard reagents.[31,32] The reaction takes place in several stages and makes it possible to obtain a DS with an unsubstituted or substituted methylene group:

$$R_FSO_2F + RCH_2MgX \xrightarrow[25°C]{THF} (R_FSO_2)_2CHR\ ;$$
$$R = H, Me;\ R_F = CF_3, C_4F_9, C_8F_{17}\ .$$

Methanedisulphonyl fluoride has been synthesised by the reaction of methionic acid chloride (methanedisulphonyl chloride) with anhydrous zinc fluoride:[33,34]

$$CH_2(SO_2Cl) + ZnF_2 \rightarrow CH_2(SO_2F)_2\ .$$
$$(VII)$$

Cyclic DS are usually obtained by oxidising 1,3-dithiacycloalkanes, which are in their turn synthesised from the corresponding αω-dithiol and a carbonyl compound (an aldehyde or ketone). The use of formaldehyde or its trimer with subsequent oxidation lead to cyclic 1,3-disulphones with a free methylene group:[35]

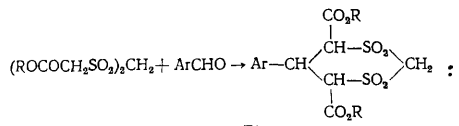


$$R^1, R^2 = H, Alk;\ n = 2-4\ .$$

The reaction of αω-dihalogenoalkanes with sodium thiosulphate is a convenient method of synthesis of 1,3-dithiacycloalkanes.[36] The polymethylenebisthiosulphonate formed as an intermediate reacts with carbonyl compounds to form 1,3-dithiacycloalkanes, which are then oxidised by hydrogen peroxide to cyclic 1,3-disulphones:[37]

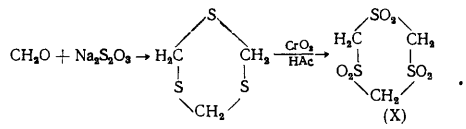
$$X-(CH_2)_n-X + Na_2S_2O_3 \rightarrow (CH_2)_n(SSO_2ONa)_2 \xrightarrow{R^1COR^2} (VIII) \xrightarrow{[O]} (IX)\ ;$$
$$R^1, R^2 = Alk;\ X = Cl, Br;\ n = 2-4\ .$$

Cyclic 1,3-disulphones containing oxygen atoms in the ring have been synthesised by an analogous procedure.[38] A method of synthesis of ring-substituted 1,3-dithiane 1,1,3,3-tetroxides with a free methylene group by the condensation of bis(alkoxycarbonylmethanesulphonyl)methane with various aldehydes in the presence of ammonium acetate has been published recently:[39]



R = Me, Et .

*sym*-Trithianes, which are products of the interaction of aldehydes or ketones with hydrogen sulphide,[40,41] are readily oxidised to cyclic trisulphones containing three free or substituted methylene groups. 2,4,6-Trimethylene-1,3,5-trisulphone (TTS) (X) has been most thoroughly investigated. It is usually synthesised by the reaction of formaldehyde with sodium thiosulphate[42,43] and the oxidation of the tris-sulphide formed by chromium trioxide in acetic acid:



2,4,6-Tri(methylmethylene)-1,3,5-trisulphone (TMTS) has been synthesised by the same method.[45]

## 2. Geminal Trisulphones

Two methods of synthesis of geminal trisulphones have been described in the literature. Symmetrical aliphatic and aromatic TS are obtained by oxidising orthothioesters:[46]

$$3RSH \xrightarrow{HCOOH} CH(SR)_3 \xrightarrow{[O]} CH(SO_2R)_3 ;$$
$$R = Alk, Ar . \qquad (XI)$$

The orthothioesters are synthesised by the Houben method.[47] Owing to their high tendency to hydrolyse, the oxidation is carried out very cautiously using peracetic[48] and perphthalic[22] acids or an alkaline solution of potassium permanganate[48] as oxidants.

Owing to the low yields of the TS, this method of their synthesis has not been widely employed. A more convenient procedure for the synthesis of TS, both symmetrical and mixed, involves the introduction of an alkylthio- or arylthio-group into the molecule of bis(alkanesulphonyl)- or bis-(arenesulphonyl)-methane and its subsequent oxidation:[22,49,50]

$$(I) \xrightarrow{R^1SCl(RSO_2SR^1)} (RSO_2)_2CHSR^1 \xrightarrow{[O]} (RSO_2)_2CHSO_2R^1 ;$$
$$(XII)$$
$$R, R^1 = Alk, Ar .$$

The reaction of alkanesulphonyl chlorides with TS in the presence of alkali metal alkoxides is a convenient method of synthesis of TS:[8,22,25,51]

$$(I) \xrightarrow[EtONa]{AlkSO_2Cl} (XII) ;$$
$$Alk = Me, Et, PhCH_2 .$$

Many of the TS described in the literature, including those with a chiral carbon atom in the methylidyne group, have been synthesised by this method in satisfactory yields.[22,51] A limitation of this method consists in the impossibility of synthesising TS with three aromatic substituents, since arenesulphonyl chlorides do not enter into this reaction being weak electrophiles.

Methanetrisulphonyl fluoride has been obtained by treating methanetrisulphonic acid with sulphur tetrafluoride:[34]

$$HC(SO_3H)_3 \xrightarrow[50\,^\circ C,\ 2\ h]{SF_4,CH_2Cl_2} HC(SO_2F)_3$$
$$(XIII) .$$

## 3. Other Alkanes with Geminal Sulphonyl Groups

Alkanes (ethane, propane, etc.) containing geminal sulphonyl groups (GSG) at one end of the chain are obtained by alkylating DS having the necessary set of alkane- or arene-sulphonyl groups:[23,52]

$$(I) + R^1X \xrightarrow[EtOH]{EtONa} (RSO_2)_2CHR^1 ;$$
$$(XIV)$$
$$R = Me, Ph; R^1 = Me, Et; X = Hal, p\text{-}MeC_6H_4SO_3 .$$

The ease of the alkylation of the DS makes it possible to synthesise alkanes containing GSG in the middle of the aliphatic chain by this procedure:[52]

$$(I) + 2Me(CH_2)_nX \xrightarrow[EtOH]{EtONa} Me(CH_2)_nC(SO_2R)_2(CH_2)_nMe ;$$
$$X = Hal, n = 0, 1, 2 .$$

Certain ethane derivatives containing GSG are obtained analogously to disulphonylethane (I) by employing acetaldehyde instead of formaldehyde:[22]

$$2RSH + MeCHO \xrightarrow{H^+} (RS)_2CHMe \xrightarrow[HAc]{H_2O_2} (XIV) ;$$
$$R^1 = Me$$
$$R = Me, Ph .$$

1,1,2,2-Tetrakis(methanesulphonyl)-1,2-bis(methanesulphonylthio)ethane has been obtained by the reaction of thiophosgene with sodium methanesulphinate.[53]

The Michael reactions of DS and TS with methyl vinyl sulphone[54] or 1,1-bis(arenesulphonyl)ethylenes lead to polysulphonylpropanes (XV)–(XVII). Compounds (XVII) have also been obtained by the reaction of DS with paraformaldehyde in the presence of bases:[55–59]

$$\underset{(I)}{(ArSO_2)_2CH_2} + CH_3SO_2CH{=}CH_2 \xrightarrow{EtONa} \underset{(XV)}{(ArSO_2)_2CHCH_2SO_2Me} ;$$
$$\underset{(XII)}{(ArSO_2)_2CHSO_2Me} + \underset{}{(ArSO_2)_2C{=}CH_2} \xrightarrow{F^-} \underset{(XVI)}{(ArSO_2)_2CHCH_2C(SO_2Ar)_2SO_2Me};$$
$$\underset{(I)}{(ArSO_2)_2CH_2} \xrightarrow[CH_2O]{F^-} \underset{(XVII)}{[(ArSO_2)_2CH]_2CH_2} .$$

A pentane containing four benzenesulphonyl groups at the C(1) and C(5) atoms has been described.[57]

## 4. Unsaturated Compounds

Ethylenes with GSG have been described comparatively recently.[56,58,60,61] They were obtained by the thermal decomposition of Mannich bases obtained by condensing DS, formaldehyde, and a secondary amine (usually piperidine or pyrrolidine):

$$(I) + CH_2O + HNC_5H_{10} \rightarrow (RSO_2)_2CHCH_2NC_5H_{10} \xrightarrow[80\,^\circ C,\ 3\ h]{HCl} (RSO_2)_2C{=}CH_2 ;$$
$$(XVIII)$$
$$R = Alk, Ar.$$

The condensation of aromatic DS with aromatic aldehydes usually leads to 1,1,2-trisubstituted ethylenes:[60]

$$(PhSO_2)_2CH_2 \xrightarrow{PhCHO} (PhSO_2)_2C{=}CHPh .$$
$$(XIX)$$

Aliphatic aldehydes condensed in this way give rise to isomerisation products together with normal products.[60] The reaction of bis(ethanesulphonyl)methane with benzaldehyde is accompanied by a rearrangement with degradation of the geminal functional group.[62]

The fluorine-containing 1,1-bis(ethanesulphonyl)-2,2-bis(trifluoromethyl)ethylene has been obtained by oxidising a fluorine-containing thioketal with trifluoroperacetic acid:[63]

$$(CF_3)_2C{=}C(SEt)_2 \xrightarrow{CF_3COOOH} (CF_3)_2C{=}C(SO_2Et)_2 .$$

The majority of ethylenes with 2,2-GSG containing reactive functional groups at C(1) were discovered after the successful development of the reaction of DS with ethyl orthoformate, which made available 2,2-disulphonyl-substituted ethyl vinyl ethers (XX):[62,64,65]

$$(I) + CH(OEt)_3 \xrightarrow[Ac_2O]{ZnCl_2} \underset{(XX)}{(RSO_2)_2C{=}CHOEt} ;$$
$$R = Alk, Ar .$$

The nucleophilic exchange of the ethoxy-groups, which takes place readily in these compounds, makes it possible to synthesise a wide variety of functional derivatives of ethylenes with 2,2-GSG.[64,65]

Polysulphonylethylenes were unknown until recently despite repeated attempts at their synthesis.[66-68] The report[69] of the synthesis of tetrakis(2-chloroethylsulphonyl)-ethylene [69] proved to be erroneous. Even the synthesis of the intermediate tetrakis(alkylthio)- and tetrakis(arylthio)-ethylenes presented considerable difficulties.[70,71] It was not until the end of the 1970's that a convenient and highly effective method was proposed for the synthesis of unsaturated tetrakis-sulphides from tetrachloroethane and thiolates in aprotic solvents (DMF, DMSO, HMP, etc.), significantly accelerating nucleophilic exchange, which made compounds of this class available:[72,73]

$$Cl_2C{=}CCl_2 \xrightarrow[DMF,\ DMSO,\ HMP]{RS^-} (RS)_2C{=}C(SR)_2 ;$$
$$R = Alk, Ar .$$

This reaction as a rule involves the formation of 10–15% of tris-derivatives. Tris- and tetrakis-sulphonylethylenes (TSE) were obtained by the same investigators[74] by oxidising the corresponding tetrakis-sulphides with trifluoroperacetic acid in methylene chloride:

$$(RS)_2C{=}C(SR)_2 \xrightarrow[CH_2Cl_2]{CF_3CO_3H} \underset{(XXI)}{(RSO_2)_2C{=}C(SO_2R)_2} .$$

Propenes with GSG have been synthesised[64,75,76] by condensing ethyl vinyl ethers containing geminal electron-accepting groups (one of which is the sulphonyl group) with DS in the presence of sodium alkoxide:

$$(I) + \begin{matrix} ArSO_2 \\ X \end{matrix}\!\!>\!C{=}CHCOEt \xrightarrow[EtOH]{EtONa} \begin{matrix} ArSO_2 \\ X \end{matrix}\!\!>\!C{=}CHCH(SO_2R)_2 ;$$
$$(XXII)$$
$$X = COPh, CN, R = Alk, Ar .$$

It is striking that the synthesis of 1,1,3,3-tetrasulphonylpropenes (XXII, X = $RSO_2$) by this procedure using 2,2-disulphonyl-substituted ethyl vinyl ethers is unsuccessful because of the high rate of the competing reaction involving the dissociation of the electron-deficient double bond in these ethers.

## III. STRUCTURE AND PHYSICAL PROPERTIES

Geminal sulphones are high-melting colourless crystalline substances. They are insoluble in water; DS and TS with an unsubstituted methylidyne group dissolve in aqueous solutions of alkali or sodium carbonate.

The structure of tris(methanesulphonyl)methane has been determined by X-ray diffraction. The S–C–S angles (110.8 ± 0.4°) proved to be close to the tetrahedral value. The central C–S bonds are formally single with a length of 1.83 + 0.01 Å. The lengths of the other bonds are 1.43 ± 0.01 Å for S=O and 1.73 ± 0.02 Å for S–$CH_3$.[77,78] The structures of bis(*p*-bromobenzenesulphonyl)methane [79] and 2-(3-piperidinopropyl)-1,3-dithiane 1,1,3,3-tetraoxide [80] have been determined by X-ray diffraction.

The nature of the S=O bonds and the character of the interaction of the sulphonyl group with the rest of the molecule remain the most controversial questions in the chemistry of sulphones. The hypothesis that, apart from the σ-bond, there is additional $d_\pi$,$p_\pi$ bonding between the S and O atoms so that S=O should be regarded as a (σ + π)-bond and not a semipolar bond has nowadays received increasing confirmation.[81-84] The dipole moments of a series of aromatic DS [85] suggest that the transoid conformation of these compounds is most stable, but their values (4.7–5.8 Å) preclude an unambiguous conclusion about the character of the sulphur–oxygen bond. The dipole moments of a series of aromatic unsubstituted aliphatic DS have been investigated.[86,87]

The question of the character of the interaction of the $SO_2$ group with aromatic and unsaturated groups in sulphones is insufficiently clear. Analysis of the IR spectra of a large number of different diaryl sulphones led to the conclusion that there is a weak interaction between the π electrons of the rings and the S=O bonds.[88] Raman spectroscopic data for aryl cyclopropyl sulphones revealed the presence of a barrier to electronic conduction generated by $SO_2$ groups as a result, according to the authors, of the absence of free electrons in such groups.[89] A marked weakening of the electronic influence of the substituent on the absorption frequency of the $CF_3$ group has also been observed in a series of *p*-substituted trifluoromethylthiobenzenes [90] and in *m*-trifluoromethylthiostyrene on oxidation of the sulphide sulphur atom to the $SO_2$ group.[90,91] The study of the photoelectron spectra of dimethyl, methyl vinyl, and divinyl sulphones showed that in the last two compounds there is conjugation between the π MO of the vinyl group and the MO of the $SO_2$ group. The conjugation effect is insignificant (0.2–0.3 eV) and the $SO_2$ group exhibits a strong inductive effect (~1 eV).[92] The inductive constants of alkane- or arenesulphonyl substituents (σ* = 0.57–0.60), determined by Charton[93] from the $pK_a$ of aliphatic acids, also indicate a strong inductive effect of these groups. The constants σ*($SO_2CF_3$) = 0.64 and σ*($SO_2F$) = 0.86 are close to σ*[$N^+(Me)_3$] = 0.92.[94]

By virtue of the presence of characteristic intense absorption bands,[88] GS can be reliably identified with the aid of IR spectroscopy. The spectra of these compounds contain absorption bands characteristic of the S=O bond in the region of symmetrical (1120–1180 $cm^{-1}$) and asymmetric (1300–1380 $cm^{-1}$) stretching vibrations. Substituents of different nature in the rings of aromatic DS cause hardly any shift of the absorption bands of the $SO_2$ group.[28] The absorption bands of such groups in a series of unsaturated GS are in the same region.[58,63,65] The stretching vibration frequencies of the $SO_2$ groups are sensitive to the state of aggregation; they are higher by 10–20 $cm^{-1}$ for the substances in solution than in the crystalline state. The solvent as a rule removes the band splitting which is frequently observed. The study of the IR spectra of 2,2-bis(arenesulphonyl)vinyl ethyl ethers[62,65] and 1,1-bis(arenesulphonyl)ethylenes [57] yielded direct evidence for the absence of conjugation of the $SO_2$ groups with the C=C double bond. The $^1H$ NMR spectra of a series of aromatic DS have been investigated.[95] The signals of the methylene protons are manifested by a narrow unresolved peak in the range 4–4.5 p.p.m. ($CDCl_3$) or 6–6.5 p.p.m. (DMSO). The downfield shift of the signals in DMSO can be accounted for by the formation of intermolecular hydrogen bonds between the substrate and the solvent (for a more detailed discussion of this problem, see Section IV). The effective correlation of the chemical shifts of the methylene protons with the Hammett σ constants led the authors to the conclusion, without ruling out the

possibility of the transmission of the substituent effect through space, that the electronic influence is transmitted via the $SO_2$ group with the possible participation of the 3*d* orbitals of sulphur in the formation of the S=O bond and that $d_\pi, p_\pi$ conjugation is present. The $^1$H NMR spectra of polysulphonylpropanes,[55] 1,1-bis(benzenesulphonyl)-ethylene,[58] and propenes containing GSG [75] have been published. The $^{13}$C NMR spectrum of tetrakis(benzene-sulphonyl)ethylene has been published by Petukhova et al.[74]

α-Alkylated aromatic [96] and cyclic [97] DS have been used as convenient subjects for the study by $^1$H NMR of the possibility of the formation of an intramolecular hydrogen bond between the hydrogen atom of the methylidyne group and the electron-donating group in the ω-position in the aliphatic chain. The OMe, $N(Me)_2$, $N(Et)_2$, piperidino-, and morpholino-groups were used as electron donors. The presence of an intermolecular hydrogen bond in compounds with two and three carbon atoms in the aliphatic chain has been demonstrated from the shift of the methylidyne proton signal.

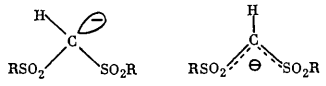
The mass-spectra of $PhCH_2SO_2CH_2SO_2Me$ have been investigated in order to confirm the mechanism of the rearrangement, analogous to the Ramberg–Bäcklund reaction of α-halogenosulphones, which takes place in compounds of this series.[98] The rearrangements of monosulphones induced by electron impact have been discussed in a review.[99]

## IV. CH ACID PROPERTIES

The acid properties of DS and some of their derivatives were noted already in the first publications. Subsequently the acid properties of compounds activated by two (and more) sulphonyl groups as well as the study of factors influencing the stabilisation of the corresponding carbanions and their reactivity attracted much attention among investigators. The thermodynamic acidities of numerous DS and TS were determined experimentally, methods were developed for the generation of carbanions, and a study was made of the dependence of the reactivity of carbanions with GSG on the configuration of the carbon atom of the methylene or methylidyne group, on the molecular conformation, and on the 2*p*, 3*d* orbital interaction. The proton-donating activities of certain GS and the formation of hydrogen bonds with electron donors and their kinetic acidity were investigated.

### 1. Thermodynamic Acidity and Stabilisation of Carbanions

The reactivities of DS or TS as CH acids are determined by the ease of deprotonation (thermodynamic factor) and the rate of reaction of the carbanions formed (kinetic factor). Two extreme structures can be put forward for carbanions generated from DS–(A), where the charge is localised at the carbon atom, and (B), where the charge is fully delocalised over the sulphonyl groups:



(A) (B)

The nature of the $RSO_2$ substituents in the molecule of the initial CH acid and its geometry determine the degree of delocalisation of the charge in the carbanion. According to the molecular orbital perturbation theory, an increase in the degree of charge delocalisation entails a decrease of the energy of the highest occupied molecular orbital, an increase of the stability of the carbanion, a decrease of its nucleophilicity, and an increase of the acidity of the CH acid.

Titrimetric determination of the dissociation constants of DS have become part of the practical research routine after the introduction of electrochemical titration methods in non-aqueous media (potentiometry and conductimetry). Owing to the inadequate solubility in water of the majority of GS, the dissociation constants of many of them have been determined by potentiometric titration in organic solvents. The available literature data and the experimental acidity constants of DS in aqueous solutions are limited (Table 1).

Table 1. The acidity constants of DS ($H_2O$, 25 °C).

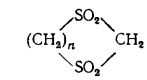
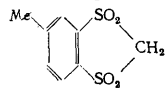
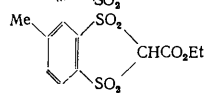
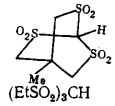
| Compound | $pK_a$ | Refs. |
|---|---|---|
| $(MeSO_2)_2CH_2$ | 12.50 | [100] |
| $(PhSO_2)_2CH_2$ | 11.21;11.50 | [100,101] |
| $(PhOSO_2)_2CH_2$ | 7.60 | [102] |
| | 13.9 (*n*=2) | [100] |
|  | 12.61 (*n*=3) | [100] |
| | 11.75 (*n*=4) | [100] |
| | 10.99 (*n*=5) | [100] |
|  | 13.00 | [101] |
|  | 3.35 | [101] |
| $(PhSO_2)_2CHCO_2Et$ | 4.60 | [101] |
|  | 3.30 | [103] |
| $(EtSO_2)_3CH$ | ≪3.30 | [103] |
| $(CF_3SO_2)_2CH_2$ | 0.23 | [32] |

Table 2. The acidity constants of DS (DMF, 25 °C).[106,107]

| No. | Compound | $pK_a$ |
|---|---|---|
| 1 | $(PhSO_2)_2CH_2$ | 13.80 |
| 2 | $(p\text{-}MeC_6H_4SO_2)_2CH_2$ | 14.16 |
| 3 | $(p\text{-}ClC_6H_4SO_2)_2CH_2$ | 12.85 |
| 4 | $(p\text{-}O_2NC_6H_4SO_2)_2CH_2$ | 10.43 |
| 5 | $(4\text{-}EtNH\text{-}3\text{-}O_2NC_6H_3SO_2)_2CH_2$ | 13.84 |
| 6 | $(4\text{-}PhNH\text{-}3\text{-}O_2NC_6H_3SO_2)_2CH_2$ | 13.25 |
| 7 | $(4\text{-}Me\text{-}3\text{-}O_2NC_6H_3SO_2)_2CH_2$ | 12.30 |
| 8 | $(4\text{-}Cl\text{-}3\text{-}O_2NC_6H_3SO_2)_2CH_2$ | 11.08 |
| 9 | $(4\text{-}HO\text{-}3\text{-}O_2NC_6H_3SO_2)_2CH_2$ | 11.53 |
| 10 | $(p\text{-}MeC_6H_4SO_2)_2CHCSNHC_6H_4Me\text{-}p$ | 9.15 |
| 11 | $(p\text{-}MeC_6H_4SO_2)_2CHCSNHC_6H_4OEt\text{-}p$ | 9.32 |
| 12 | $(p\text{-}MeC_6H_4SO_2)_2CHCSNHPh$ | 8.80 |
| 13 | $(p\text{-}MeC_6H_4SO_2)_2CHCSNHC_6H_4Cl\text{-}p$ | 8.25 |
| 14 | $(p\text{-}MeC_6H_4SO_2)_2CHCSNHC_6H_4Br\text{-}p$ | 8.20 |
| 15 | $(p\text{-}MeC_6H_4SO_2)_2CHCSNHC_6H_4I\text{-}p$ | 8.05 |
| 16 | $(p\text{-}MeC_6H_4SO_2)_2CHCSNHC_6H_4NO_2\text{-}p$ | 7.36 |

The principal relations between the conformation, configuration, and stability of the α-sulphonyl carbanion have been formulated in Cram's well known monograph[105] on the basis of the conformations of the α-sulphonyl-carbanion calculated by the molecular orbital method[104] and also the analysis of the thermodynamic stabilities of

sulphones (Table 1) and certain phenols with the $SO_2R$ group.[100]

The acidity constants of GS have been determined by potentiometric titration in DMF [106,107] (Table 2). The $pK_a$ values (compounds 1–4 and 5–9, Table 2) are satisfactorily correlated with the $\sigma$ constants of the substituent ($\rho = 2.094$ and 2.557, $r = 0.995$ and 0.996, and $s = 0.192$ and 0.100 respectively).

Table 3. The acidity constants of substituted DS and TS (96% alcohol, 25 °C).[25]

| Compound | $pK_a$ | Compound | $pK_a$ |
|---|---|---|---|
| $PhSO_2CH(SO_2Me)CN$ | 2.84 | $p$-$MeC_6H_4SO_2CH(SO_2Me)COPh$ | 5.81 |
| $p$-$MeC_6H_4SO_2CH(SO_2Me)CN$ | 2.78 | $p$-$ClC_6H_4SO_2CH(SO_2Me)COPh$ | 4.77 |
| $p$-$ClC_6H_4SO_2CH(SO_2Me)CN$ | 2.83 | $PhSO_2CH(SO_2Me)COOEt$ | 6.06 |
| $(EtSO_2)_2CHSO_2Me$ | 2.99 | $p$-$MeC_6H_4SO_2CH(SO_2Me)COOEt$ | 6.36 |
| $(PhSO_2)_2CHSO_2Me$ | 3.00 | $p$-$ClC_6H_4SO_2CH(SO_2Me)COOEt$ | 5.24 |
| $(p$-$MeC_6H_4SO_2)_2CHSO_2Me$ | 3.06 | $PhSO_2CH(SO_2Me)CONH_2$ | 7.51 |
| $(p$-$ClC_6H_4SO_2)_2CHSO_2Me$ | 2.95 | $p$-$MeC_6H_4SO_2CH(SO_2Me)CONH_2$ | 7.65 |
| $PhSO_2CH(SO_2Me)COPh$ | 5.32 | $p$-$ClC_6H_4SO_2CH(SO_2Me)CONH_2$ | 7.00 |

Table 4. The acidity constants of substituted propenes $p$-$RC_6H_4SO_2C(CN)=CHCH(SO_2R^1)_2$ (25 °C).[75,76]

| R | $R^1$ | $pK_a$ | |
|---|---|---|---|
| | | acetone | 96% alcohol |
| H | Et | −0.94 | 2.76 |
| Me | Et | −1.10 | 2.76 |
| Cl | Et | −1.57 | 2.70 |
| H | Ph | −0.94 | 2.81 |
| H | $p$-$MeC_6H_4$ | −0.54 | — |
| H | $p$-$ClC_6H_4$ | −1.90 | — |
| Me | Ph | −0.74 | 2.81 |
| Me | $p$-$MeC_6H_4$ | −0.49 | — |
| Cl | $p$-$ClC_6H_4$ | −1.29 | 2.79 |
| Cl | $p$-$MeC_6H_4$ | −1.00 | — |

The character of the change in the acid properties of asymmetric DS when the hydrogen atom of the methylene group is substituted by a third electron-accepting group has been investigated[25] (Table 3) and the authors established that the electronic nature of the substituents in the $p$-position in the aromatic ring of the $SO_2Ar$ group has little influence on the acidity of the compound, while the introduction of a third electron-accepting substituent at the methylidyne carbon atom greatly increases it. In terms of their effect on the acidity of $MeSO_2CH(R)SO_2Ph$, the substituents at the α-carbon atom can be arranged in the sequence $CN \geq SO_2Ph \gg COPh > COOEt > CONH_2$. The acid properties of propenes with GSG (Table 4) have been studied in order to compare them with the acidity of DS containing electron-accepting substituents in the α-position (Table 3) and in order to elucidate the nature of the activating effect of the vinyl group with two electron-accepting substituents at the β-carbon atom.[75,76] The propenes (Table 4) are strong CH acids. The delocalisation of the charge and the stabilisation of the corresponding carbanions are achieved by virtue of the $-I$ effects of the arene- or alkane-sulphonyl groups and the $-M$ effect of other electron-accepting substituents.

The first quantitative study of the selective solvation of aliphatic DS by $^1H$ NMR in mixed aqueous binary systems (1,4-dioxan–$H_2O$, 1,3-dioxan–$H_2O$, and dimethoxyethane–$H_2O$) was carried out by Remerie and Engberts.[108]

## 2. The Proton-Donating Capacity and Kinetic Acidity

Studies carried out during the last decades have shown that the C–H groups polarised by strong electron-accepting substituents form hydrogen bonds (HB) as proton donors.

Table 5. Thermodynamic characteristics of the hydrogen bonds with DMSO, acetone, and pyridine.[109,110]

| No. | Compound | DMSO | | Acetone | | |
|---|---|---|---|---|---|---|
| | | $-\Delta H$, kJ mol$^{-1}$ | $-\Delta S$, J mol$^{-1}$K$^{-1}$ | $-\Delta H$, kJ mol$^{-1}$ | $-\Delta S$, J mol$^{-1}$K$^{-1}$ | $pK_a$ |
| 1 | $(PhSO_2)_2CH_2$ | 9.2 | 20.9 | 12.6* | 31.0* | 11.2 |
| 2 | $p$-$ClC_6H_4SO_2CH(COPh)SO_2Me$ | 13.8 | 23.0 | 10.5 | 20.9 | 4.77 |
| 3 | $PhSO_2CH(COPh)SO_2Me$ | 14.2 | 25.5 | 9.6 | 18.0 | 5.32 |
| 4 | $p$-$MeC_6H_4SO_2CH(COPh)SO_2Me$ | 12.6 | 21.3 | 10.0 | 21.3 | 5.81 |
| 5 | $p$-$ClC_6H_4SO_2CH(COOEt)SO_2Me$ | 10.9 | 16.7 | 11.3 | 21.3 | 5.24 |
| 6 | $PhSO_2CH(COOEt)SO_2Me$ | 10.9 | 18.8 | 9.6 | 23.4 | 6.06 |
| 7 | $p$-$CH_3C_6H_4SO_2CH(COOEt)SO_2Me$ | 10.9 | 19.2 | 10.5 | 22.2 | 6.36 |

*In pyridine.

The strength of the $R_nCH_{4-n}\ldots B$ bonds depends both on the nature and number of substituents R and on the electron-donating capacity of the base B. The proton donating capacity of bis(benzenesulphonyl)methane in the formation of HB with DMSO and pyridine and also of the trisubstituted methanes ($MeSO_2$) ($p$-$XC_6H_2SO_2$)CHR in similar reactions with acetone and DMSO has been studied by $^1H$ NMR in the series of GS.[110] It follows from the results presented in Table 5 that the enthalpy of the HB formed by the compounds investigated with DMSO is in the range 9.2–14.2 kJ mol$^{-1}$. The strength of the HB between trisubstituted methanes and DMSO is higher, in conformity with their more acid character, than for bis(benzenesulphonyl)methane. However, in the series of trisubstituted methanes there is no general relation between the quantities $K_a$ and $\Delta H$ embracing all the compounds investigated. The kinetics and thermodynamics of proton transfer from trisubstituted methane to γ-collidine have been investigated by $^1H$ NMR in $CD_2Cl_2$ by Pogorelyi et al.[111,112], while the kinetics of the proton exchange in the trisubstituted methane–triethylamine systems have been investigated by the same workers in Ref. 113. According to their data,[111] the proton transfer to γ-collidine is preceded by the formation of hydrogen-bonded complexes:

$$\geq CH + N \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \geq CH \ldots N \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \geq C^- \ldots HN^+ \diagup$$

The proton transfer is completed by the formation of an ion pair which does not dissociate in $CD_2Cl_2$ (having a low dielectric constant ε) and is a kinetically independent species. The results of calculations of the kinetic and thermodynamic characteristics are presented in Table 6.

According to Table 6, the activation energies for deprotonation $E_+$ are significantly smaller for all the compounds investigated than the values of $E_-$ characterising

the reverse process; this shows that the proton abstraction reaction is exothermic ($\Delta Q < 0$). The characteristics of the equilibrium ($\lg K$ and $\Delta Q$) vary in parallel with the equilibrium acidity ($pK_a$). The authors[111] believe that, since the degree of delocalisation of the free electron pair in the carbanion is high in the DS investigated, the transition state of the reaction is reactant-like according to Hammond's postulate, i.e. the degree of proton transfer in the transition state is low. The conjugation effect is therefore manifested mainly in the anion and not in the transition state of the deprotonation reaction of the CH acid, which induces an increase of $E_-$. The small change in $E_+$ in the series of compounds investigated is evidence for an insignificant difference in the effect of the substituents PhCO and COOEt on the polarity and strength of the C–H bond. On the other hand, in conformity with their mesomeric effects, these substituents affect significantly the protonation energy of the carbanion $E_-$. In the series of compounds with identical R, the substituents X also have a greater effect on $E_-$ than on $E_+$. Consequently substituents influence mainly the kinetic characteristics of the protonation of the carbanion and have a very weak effect on the rate of deprotonation of the acid. Analysis of the relations between $pK_a$, $E_+$, $E_-$, and $k_+$ (the kinetic acidity of $R_3CH$) or $k_-$ (the kinetic basicity of $R_3C^-$), carried out in the above study,[111] permits the conclusion that the equilibrium acidity of $R_3CH^-$ is determined mainly by the stability of the carbanion and depends to a much lesser extent on the strength and polarity of the C–H bonds.

Table 6. Thermodynamic and kinetic characteristics of the proton transfer from the DS $p$-$XC_6H_4SO_2CH(R)SO_2Me$ to $\gamma$-collidine.[111]

| No. | X | $pK_a$ (alcohol) | $\lg K^{293}$ | $-\Delta Q$, kJ mol$^{-1}$ | $-\Delta S$, J mol$^{-1}$K$^{-1}$ | $\lg k_+^{293}$ | $E_+$, kJ mol$^{-1}$ | $\lg A_+$ | $\lg k_-^{293}$ | $E_-$, kJ mol$^{-1}$ | $\lg A_-$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | PhCOCl | 4.77 | 2.8 | 52 | 120 | 3.8 | 22 | 8 | 1.0 | 74 | 14 |
| 2 | PhCOMe | 5.81 | 1.7 | 37 | 92 | 3.3 | 27 | 8 | 1.6 | 63 | 13 |
| 3 | COOEtCl | 5.24 | 1.9 | 32 | 76 | 5.7 | 18 | 9 | 3.8 | 51 | 13 |
| 4 | COOEtMe | 6.36 | 0.9 | 24 | 62 | 5.1 | 17 | 8 | 4.2 | 41 | 12 |

The observed relations were interpreted by the same workers[112] in terms of the Bell–Evans–Polanyi potential curves, which confirmed that there is no general relation between the thermodynamic or kinetic acidity and the strength of the HB with DMSO ($\Delta H$) in the series of trisubstituted methanes with GSG.

The experimental data obtained in the study of the kinetics of proton exchange in the $(MeSO_2)(p\text{-}XC_6H_4SO_2)CHR$–triethylamine (R = COPh or COOEt) systems by $^1H$ NMR in $CD_2Cl_2$ made it possible to establish the mechanism of the process.[113]

## V. REACTIVITY

The reactivities of the majority of GS are determined by the activating influence of the sulphonyl groups. DS and TS as well as certain higher alkanes activated by GSG as CH acids are involved in the chemical reactions as a rule in the form of the conjugated bases (carbanions), so that electrophilic substitution reactions are characteristic of the compounds enumerated above. The activation of the double bond in unsaturated GS is responsible for the ease of the nucleophilic substitution and addition reactions in the series of these compounds.

### 1. Electrophilic Substitution Reactions

(*a*) *Salts and complex formation.* Alkali metal salts are formed when DS are treated with the corresponding hydroxides or alkoxides:[12,52,114]

$$\underset{\text{(I)}}{} + MOH \rightarrow \underset{\text{(XXIII)}}{(RSO_2)_2\bar{C}HM^+} + H_2O\ ;$$

$$R = Alk, Ar;\ M = Li, Na, K, NH_4\ .$$

In the series of DS the second hydrogen atom of the methylene group is not substituted by a metal even when strong bases (BuLi) are used.[115] The silver salt of methanedisulphonyl fluoride was isolated after prolonged refluxing of the latter with silver oxide in anhydrous ether in the presence of a zeolite.[34] Bis(benzenesulphonyl)-methylmagnesium bromide has been obtained by the reaction of the corresponding DS with butenylmagnesium bromide in ether.[115] The salt-forming reaction between bis(benzenesulphonyl)methane and monoethanolamine has been investigated.[117]

Being stronger CH acids, trisulphones form salts with alkali metal or alkaline earth metal hydroxides, alkoxides, and carbonates[118] and also with organic bases.[119] The salts of tris(methanesulphonyl)methane with the $NH_4^+$, $Li^+$, $K^+$, $Rb^+$, $Cs^+$, and $Tl^+$ anions have been obtained for crystallographic analysis.[120] The salts $M[C(SO_2Et)_3]_2.6H_2O$ (M = $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$, or $Cd^{2+}$) have been prepared by heating aqueous suspensions of the metal carbonate and the TS. The manganese and cobalt salts react with pyridine (Py) and phenanthroline (L) to form the complexes $M(Py)_2.[C(SO_2Et)_3]_2$ and $[ML]_3.[C(SO_2Et)_3]_2$.[121]

In order to investigate the reactivities of the metal cation–carbanion ion pairs, the complexes of the sodium salts of TS with 15-crown-5-ether and of the potassium salt of bis-(benzenesulphonyl)methane with 18-crown-6-ether were synthesised.[122] These complexes proved to be relatively unreactive; this can be explained by the formation of a close ion pair comprising the anion and a complex cation, which creates steric hindrance to attack by the electrophile. TS give rise to high yields of tetra-alkylammonium salts on interaction with tetra-alkylammonium halides in the $CH_2Cl_2$–$H_2O$ two phase system in the presence of alkali.[123]

(*b*) *Alkylation and sulphenylation.* The ion pair comprising aromatic and aliphatic DS $(RSO_2)_2CH^-M^+$ (XXIII) (M = alkali metal) is readily alkylated by alkyl halides to form mono- and di-alkyl derivatives:

$$\text{(XXIII)} \xrightarrow{R^1X} \underset{\text{(XIV)}}{(RSO_2)_2CHR^1}\ ;$$

$$\text{(XXIII)} \xrightarrow{2R^1X} (RSO_2)_2CR^1_2\ ;$$

$$R^1 = Alk;\ X = Cl, Br, I\ .$$

2,2-Bis(benzenesulphonyl)propane has been isolated after the alkylation of bis(benzenesulphonyl)methane with methyl iodide in absolute alcohol in the presence of sodium ethoxide:[52] the analogous reaction with benzyl chloride (THF–hexane, BuLi) yields the monoalkylation product.[115] The silver salts of methanedisulphonyl fluoride[34] and bis-(trifluoromethanesulphonyl)methane[32] react with one molecule of the alkylating agent, while cyclic trimethylene

trisulphone (X) reacts with alkyl iodides in an aqueous-alcoholic alkaline solution to form hexa-alkyl-substituted derivatives.[45,124]

Cyclic alkylation products, derivatives of cyclopentane, have been obtained by the reaction of the sodium salts of aromatic, aliphatic, and cyclic DS with dimethylvinylsulphonium bromide in anhydrous methanol:[125]

$$(XXIII) + CH_2{=}CH\overset{+}{S}Me_2Br^- \rightarrow \left|\begin{array}{l}SO_2R\\SO_2R\end{array}\right. \xrightarrow{HI} (RSO_2)_2CH(CH_2)_2I \ ;$$

57%

R = Me, Et, Ph or R, R = $-CH_2CH_2-$ .

When cyclopropanes are refluxed with hydriodic acid, 1,1-disubstituted 3-iodopropanes are formed. 1,1-Bis(benzenesulphonyl)cyclopropane reacts as the 1,3-dipolar ion:[126]

$$\left|\begin{array}{l}SO_2Ph\\SO_2Ph\end{array}\right. \rightarrow [\overset{+}{C}H_2CH_2\overline{C}(SO_2Ph)_2] \ ;$$

$$RXH + \left|\begin{array}{l}SO_2Ph\\SO_2Ph\end{array}\right. \xrightarrow{DMF} RXCH_2CH_2CH(SO_2Ph)_2 \rightarrow$$

$$\xrightarrow[NaH]{R^1Hal} RXCH_2CH_2C(R^1)(SO_2Ph)_2 \ ;$$

R = Ar, $R^1$ = Alk, X = S, O .

In the presence of sodium alkoxide, methylthiobis(methanesulphonyl)methane is alkylated by allyl bromide:[120]

$$(MeSO_2)_2CHSMe \xrightarrow[EtONa]{CH_2{=}CHCH_2Br} (MeSO_2)_2C(SMe)CH_2CH{=}CH_2 \ .$$

The alkylation of bis(benzenesulphonyl)methane by dienes in the presence of catalysts has been investigated.[127]

In the study of the reaction of phenylmethanesulphonyl fluoride with phenyl-lithium, Shirota et al.[128] isolated α-benzenesulphonyl-α-phenylmethanesulphonyltoluene, whose formation can be explained by the competition of two processes occurring in this reaction: nucleophilic substitution at the sulphur atom and metallation of the methylene group:

$$PhCH_2SO_2F \xrightarrow{PhLi} PhCH_2SO_2Ph + PhCHLiSO_2F \ ;$$

$$PhCH_2SO_2Ph \xrightarrow{PhLi} PhCHLiSO_2Ch \xrightarrow{PhCH_2SO_2F} PhCH_2SO_2CH(Ph)SO_2Ph.$$

Disulphones are readily alkylated by αβ-unsaturated compounds under the conditions of the Michael reaction. Aliphatic DS combine with two molecules of an αβ-unsaturated compound and aromatic DS combine with one such molecule.[54,129,130] γγ-Bis(arenesulphonyl)butyric and 4,4-bis(ethanesulphonyl)pimelic acid and many of their derivatives have been synthesised[129,130,131] by the reaction involving the addition of acrylonitrile to aromatic DS [129] and bis(ethanesulphonyl)methane.[130] The reactions of trimethylenetrisulphone (X) [132] and its derivatives[133] with acrylonitrile, ethyl acrylate, and 2-vinylbenzothiazole have been investigated. The alkylation of bis(benzenesulphonyl)-methane by the salt of a Mannich base, namely the hydrochloride of 1-dimethylamino-2-(2-thenoyl)ethane, which takes place with elimination of the amine, has been described.[134]

In contrast to DS, trisulphones are alkylated with difficulty, which can apparently be accounted for by the much lower nucleophilicity of their carbanions. The yield of 1,1,1-tris(methanesulphonyl)ethane in the reaction of the sodium salt of tris(methanesulphonyl)methane with methyl iodide is extremely low (3.6%).[120] The interaction of the silver salt of tris(benzenesulphonyl)methane with methyl iodide[118] and bromotris(methanesulphonyl)methane with methylmagnesium bromide[120] does not lead to methylation products. The products of the alkylation of TS are therefore obtained by alkylating alkyl- or aryl-thio-derivatives of DS or by sulphenylating alkylated DS with subsequent oxidation of the reaction products:[120]

$$\left.\begin{array}{l}(MeSO_2)_2CHSMe \xrightarrow{MeI}\\(MeSO_2)_2CHMe \xrightarrow{MeSSO_2Me}\end{array}\right] \rightarrow (MeSO_2)_2C(Me)SMe \rightarrow$$

$$\xrightarrow{H_2O_2} (MeSO_2)_3CMe.$$

An interesting method has been developed for the ethylation of TS with a high yield.[135] It has been observed that, after prolonged heating with ethyl orthoformate in the presence of acetic anhydride and $ZnCl_2$, TS give rise to the diethylacetals of 1,1,1-tris-sulphonylacetaldehydes, which are unstable and are rapidly cleaved to 1,1,1-tris-sulphonylpropanes and ethyl formate:

$$(RSO_2)_3CH \rightarrow [(RSO_2)_3CCH(OEt)_2] \rightarrow (RSO_2)_3CEt + HCOOEt \ ;$$

R = Alk, Ar .

A direct method for the arylation of the methyl group in DS has not been described. Monoaryl derivatives are usually synthesised in accordance with the scheme[29]

$$ArCHO + 2RSH \rightarrow ArCH(SR)_2 \xrightarrow[HAc]{H_2O_2} ArCH(SO_2R)_2 \ ;$$

R = Alk, Ar.

DS and TS are sulphenylated by sulphenyl halides or the thioesters of sulphinic acids in an alkaline medium and the reaction proceeds as a rule more readily (particularly in the series of TS) than alkylation, since sulphenylating agents are stronger electrophiles. The reactions of DS with the thioesters of sulphinic acid[120,136,137] and sulphenyl chlorides[118,120,136] and of the silver salt of methanedisulphonyl fluoride with pentafluorobenzenesulphenyl chloride[34] have been described:

$$(I) \xrightarrow[EtONa]{R^1SCl(R^1SSO_2R^2)} (RSO_2)_2CHSR^1 \ ;$$

(XXIV)

R = Me, Ph; $R^1$ = Me, $PhCH_2$, Ph; $R^2$ = Me, Ph, $(Ph)_2CH$.

DS can be alkane- and arene-sulphenylated in steps with formation of mono- and di-thio-derivatives.[120,137] TS are sulphenylated under the same conditions.[120]

The thioarylation[138] and selenoarylation[139] of bis(benzenesulphonyl)methane has been achieved in alkaline media by treatment with diaryl sulphide selenides (ArSSeAr) and diaryl diselenides (ArSeSeAr):

$$(PhSO_2)_2CH_2 + RC_6H_4XSeC_6H_4R \xrightarrow{EtONa} (PhSO_2)_2CHXC_6H_4R \ ;$$

R = H, *m*- or *p*-Me, *o*- or *p*-Cl, *m*- or *p*-$NO_2$, *p*-Br, *p*-MeO; X = S, Se.

The alkyl- and aryl-thiomethylation of aliphatic and aromatic DS by condensation with mercaptans and formaldehyde in alkaline media has been described:[140]

$$(I) + CH_2O + R^1SH \xrightarrow{NaOH} (RSO_2)_2CHCH_2SR^1 \ ;$$

R = n-Bu, Ph, cyclohexyl; $R^1$ = alkyl, aryl.

Bis(benzenesulphonyl)methane is more reactive in this reaction than its aliphatic analogue. When the merceptan is replaced by potassium hydrogen sulphide, 1,1,5,5-tetrasulphonyl-3-thiapentanes are formed:[141]

$$(I) \xrightarrow[dioxan,MeOH,H_2O]{CH_2O,KSH} [(RSO_2)_2CHCH_2]S_2 \ ;$$

20°, 12 h, R = alkyl, aryl.

The reaction of bis(methanesulphonyl)methane with carbon disulphide in DMSO in the presence of t-BuOK (20 °C, $N_2$) and subsequent methylation of the reaction product with methyl iodide lead to 1,1-bis(methanesulphonyl)-2,2-bis(methylthio)ethylene:[68]

$$(MeSO_2)_2CH_2 \xrightarrow[t\text{-}BuOK,\ DMSO]{1)CS_2\ 2)MeI} (MeSO_2)_2C{=}C(SMe)_2 \ .$$

The hydrolysis of mono- and di-mercapto-substituted DS in the presence of bases (NaOH, piperidine) and acids (HCl, $H_2SO_4$) proceeds with successive elimination of alkyl- or aryl-thio-groups. Sulphinic acids, diaryl and dimethyl thiocarbonates, thioesters of sulphinic acids, and dialkyl disulphides have been found among the reaction products:[142]

Tris(methanesulphonyl)methanes with a substituent at the carbon atom of the methylidyne group split off one $MeSO_2$ group on heating in an alkaline medium:[120]

$$(MeSO_2)_3CX \xrightarrow{H_2O,NaOH} (MeSO_2)_2CHX + MeSO_3Na\ ;$$
$$X = Me, Ph, MeS, NO_2\ .$$

The hydrolysis of substituted tris(methanesulphonyl)-methanes in the presence of organic bases has been investigated.[143]

(c) *Halogenation. Properties of halogeno-derivatives.* In aqueous alkaline media DS and TS are halogenated by freshly prepared hypohalites,[32,46,114,118,130,144,145] while in organic solvents ($CCl_4$–$CHCl_3$ mixture,[144] acetic acid[146]) they are halogenated by elemental halogens ($Cl_2$, $Br_2$). In a series of DS the ease of the halogenation reaction creates appreciable difficulties in the synthesis of the monohalides. They are obtained by treating the substrate in dilute aqueous alkaline solutions with an equimolar amount of a hypohalite[114,130] and by halogenating a DS salt with elemental halogen in an organic solvent.[32] The monohalides of DS have also been synthesised by halogenating the esters of bis(sulphonyl)acetic acids:[26]

$$\underset{(V)}{(RSO_2)_2CHCOOR^1} \xrightarrow{Hal_2} (RSO_2)_2CHalCOOR^1 \xrightarrow[-R^1OH]{H_2O} \rightarrow (RSO_2)_2CHalCOOH \xrightarrow[-CO_2]{} \underset{(XXV)}{(RSO_2)_2CHHal}\ ;$$
$$R = Alk, Ar; Hal = Cl, Br\ .$$

The halogenation of trimethylenetrisulphone (X) in aqueous alkaline media leads to the formation of hexahalogeno-derivatives.[124,147] Disulphones containing a third electron-accepting substituent ($NO_2$, COMe) at the α-carbon atom are readily hydrogenated by hypohalites,[29,148] but the acetyl group is not then eliminated.[148]

The silver salt of methanetrisulphonyl fluoride (XIII) is brominated and iodinated in Khladon 113 with formation of tris(fluorosulphonyl)halogenomethanes.[134] tris(Fluoro-sulphonyl)iodomethane is the first iodo-derivative of DS and TS described in the literature. Halogenation with hypo-halites in an aqueous alkaline medium is a very rapid process mainly owing to the high concentration of the electrophilic $Br^+$ species and the "carbanionic state" of the substrate. Halogenation in organic solvents with elemental halogens proceed much more slowly. Tris(ethanesulphonyl)methane is brominated in acetic acid much more slowly than its potassium salt;[146] the addition of water accelerates the process.

Certain monobromo-derivatives of DS can be synthesised by disproportionation into the dibromo-derivative of the DS and an unsubstituted compound.[145] Tribromotrimethylene-trisulphone has been obtained by the reaction of TTS hexa-bromide and the unsubstituted TTS.

The equilibrium in the disproportionation reaction of a mixture of $(RSO_2)_2CH_2$ and $(RSO_2)_2CHal_2$ with formation of $(RSO_2)_2CHHal$ (R = alkyl or aryl) has been investigated.[26] It is noted that the disproportionation is reversible and proceeds more readily for the bromo-derivatives than for the chloro-derivatives.

Bromination of bis(ethanesulphonyl)methane by hypo-bromite in an aqueous alkaline medium is a reversible process; the equilibrium at 20 °C is displaced towards the formation of the dibromo-derivative:[130]

$$\underset{10\%}{(EtSO_2)_2CH_2} \underset{OH^-}{\overset{KBrO}{\rightleftarrows}} \underset{30\%}{(EtSO_2)_2CHBr} \underset{OH^-}{\overset{KBrO}{\rightleftarrows}} \underset{60\%}{(EtSO_2)_2CBr_2}\ .$$

The properties of the DS and TS halides are determined by the character of the C–Hal bond in these compounds. By virtue of the strong electron-accepting effect of the sulphonyl groups on the polarisation of the C–Hal bond, the halogen atom becomes the positive end of a dipole, assumes a cationoid character, and is capable of breaking off in the form of a cation. The mono- and di-bromo-derivatives of DS are reduced by iodide ions and can be determined quantitatively by iodometric titration.[114,130,144] The chloro-derivatives of TS also have this property:[144]

$$\rangle C{-}Hal + 2NaI \xrightarrow[25°C]{MeCN} \rangle CNa + I_2 + NaHal\ ;$$
$$Hal = Br, Cl\ .$$

DS and TS bromides are brominating agents which brominate *NN*-dimethylaniline [144] and toluene (in the presence of $AlCl_3$).[32] Hexabromotrimethylenetrisulphone has analogous properties.[149] DS mono- and di-bromides and TS chlorides and bromides react with alkalis to form DS or TS salts and hypohalites.[29,114] The hexachloro- and hexabromo-deriva-tives of trimethylenetrisulphone and the trichloro- and tribromo-derivatives of tris(methylmethylene)trisulphone react with organic bases (pyridine, αα-bipyridyl, quinoline, piperidine, and morpholine) to form complexes having the composition $(CHal_2SO_2)_3.(Nu)_n$ and $(MeCHalSO_2)_3(Nu)_n$ (Nu = organic base, $n$ = 2, 3, 5),[150,151] which have the structure of quaternary ammonium salts according to the authors. The reaction of dibromobis(methanesulphonyl)-methane with copper powder is a radical process among the products of which tris(methanesulphonyl)methane was found.[152] The monohalogeno-derivatives of DS are stronger CH acids than the unsubstituted compounds, although the acidifying effect of chlorine and bromine is small.[26] They are alkylated by diazomethane [26] and in the presence of bases they react with alkyl halides and benzenesulphenyl chloride.[26] The monochloro-derivatives of aromatic DS react in an aqueous alkaline medium with arenediazonium salts to form bis(arenesulphonyl)arylazochloromethanes [114] and they combine with acrylonitrile.[152]

$$\underset{(XXVI)}{(ArSO_2)_2CHCl} \begin{cases} \xrightarrow{ArN_2^+} (ArSO_2)_2CClN{=}NAr\ ; \\ \xrightarrow{CH_2=CHCN} (ArSO_2)_2CClCH_2CH_2CN\ . \end{cases}$$

The bromine atom in bromobis(trifluoromethanesulphonyl)-methane (XXVI) is more mobile than the hydrogen atom of the methylidyne group and is involved in the Michael reaction with αβ-unsaturated compounds instead of the latter:[32]

$$\underset{(XXVI)}{(CF_3SO_2)_2CHBr} + CH_2{=}CHR \rightarrow (CF_3SO_2)_2CHCH_2CHBrR\ ;$$
$$R = CH_2CH_2Cl\ (70\%), CH_2COOH\ (50\%), C_6H_{13}\ (32\%)\ .$$

The interaction of the bromo-derivative (XXVI) with $Na_2CO_3$ at 150 °C leads to the formation of only the sodium salt of the initial CH acid instead of the expected 1,1,2,2-tetrakis-(trifluoromethanesulphonyl)ethylene (by analogy with the reaction of bromomalonic ester).[32]

(d) *Nitration.* As shown above (Section II), DS are not nitrated at the methylene group in sulphuric acid, since a reactive carbanion is absent from such a solution. In the

series of TS, which are stronger CH acids, the carbanionic character of the carbon atom of the methylidyne group is more pronounced and they can be nitrated by the usual nitrating mixture. The low nucleophilicity of TS is compensated by the strength of the electrophile (nitronium cation). Tris-(methanesulphonyl)nitromethane has been obtained in high yields by the nitration of tris(methanesulphonyl)methane (XI) (100 °C, 15 min):[120]

$$(XI) \xrightarrow{HNO_3,H_2SO_4} (MeSO_2)_3CNO_2 .$$

It has been shown that, in the nitration of mixed TS, the aromatic ring of the arenesulphonyl groups are first nitrated, while at elevated temperatures the methylidyne group is also nitrated:[154]

$$(4\text{-}RC_6H_4SO_2)_2CHSO_2Me \xrightarrow[20°C]{HNO_3,H_2SO_4} (4\text{-}R\text{-}3\text{-}O_2NC_6H_4SO_2)_2C(NO_2)SO_2Me \ (XXVII);$$
$$R=H, Me, Cl .$$

Disulphones with a strong electron-accepting substituent at the carbon atom of the methylidyne group have acidities similar to those of TS and are nitrated under analogous conditions:[154]

$$4\text{-}MeC_6H_4SO_2CH(CN)SO_2Me \xrightarrow{HNO_3,H_2SO_4} \rightarrow 4\text{-}Me\text{-}3\text{-}O_2NC_6H_4SO_2C(NO_2)(CN)SO_2Me \ (XXVIII) .$$

The nitromethanes (XXVII) and (XXVIII) undergo hydrolytic cleavage fairly readily. As a consequence of the steric hindrance arising as a result of the repulsion of the non-bonded oxygen atoms of the sulphonyl and nitro-groups, the loss of one of these groups reduces the free energy of the system. Furthermore, the presence of four strong electron-accepting substituents increases the electronegativity of the carbon atom in the molecules of compounds (XXVII) and (XXVIII), since in each of them the substituent is somewhat less electronegative than in compounds not containing additional electron-accepting groups. The least electronegative of the four substituents (in the given case the methanesulphonyl group) can therefore be subjected to nucleophilic attack and, after the elimination of this substituent, a carbanion, stabilised by the three strong electron-accepting substituents, is formed. Even on heating in 8% aqueous $NaHCO_3$ solution, compounds (XXVII) split off the methanesulphonyl group and their treatment with freshly prepared potassium hypobromite in addition to the bromination of the intermediate carbanion.[154] On reaction with KBrO, the nitromethanes (XXVIII) also split off the $MeSO_2$ group with subsequent bromination of arenesulphonylcyanonitromethane.[154]

Hydrolysis of tris(methanesulphonyl)nitromethane in the presence of alkali affords bis(methanesulphonyl)nitromethane,[29] which reacts with chlorine and bromine in an alkaline medium[29] and reacts with $Ag_2CO_3$ as a strong CH acid to form a silver salt, which reacts with methyl iodide to produce 1,1-bis(methanesulphonyl)-1-nitroethane.[153,155]

(*e*) *Reactions with arenediazonium salts* Disulphones with a free methylene group interact with arenediazonium salts in alkaline media (pH 8–13). Depending on the structure of the DS and the diazonium salt, the reaction conditions and the reactant ratio, the interaction can proceed with formation of one or several reaction products. In the first studies devoted to this reaction,[156,157] it was already shown that aromatic TS react with diazonium salts to form the azo-coupling product

$$(I) \xrightarrow{ArN_2} (RSO_2)_2CHN{=}NAr \rightleftarrows (RSO_2)_2C{=}NNHAr ;$$
$$(XXIX) \qquad (XXX)$$
$$R=Ph .$$

An unambiguous choice between the two possible structures (XXIX) and (XXX) was not made and it was shown only later that[158] the products of the coupling of DS and other methylene compounds to diazonium salts have the hydrazone structure (XXX). In his study of the reaction of bis-(benzenesulphonyl)methane with *p*-nitrobenzenediazonium tetrafluoroborate in a weakly alkaline medium (pH 8.2), Hunig[159] isolated three reaction products: *p*-nitrophenylhydrazone of bis(benzenesulphonyl)carbonyl (XXXI), *N*-benzenesulphonyl-*N'*-(*p*-nitrophenyl)diimide (XXXII), and 5-hydroxy-1,3-di(*p*-nitrophenyl)tetrazolium betaine (XXXII):

$$(I) \xrightarrow{p\text{-}O_2NC_6H_4N_2^+BF_4^-} (PhSO_2)_2C{=}NNHC_6H_4NO_2\text{-}p + (XXXI)$$
$$+ p\text{-}O_2NC_6H_4N{=}NSO_2Ph + p\text{-}O_2NC_6H_4{-}\overset{+}{N}{-}N$$
$$(XXXII) \qquad (XXXIII)$$



A mechanism of the formation of the betaines (XXXIII) has been proposed[159] on the hypothesis of a higher reactivity of the NH group of the hydrazone (XXXI) which is formed in the first stage and reacts with a second molecule of the diazonium salt to form the "*N*-azo-derivative" (XXXIV). The rapid hydrolysis of the arenesulphonyl groups in the product (XXXIV) and subsequent ring closure lead to the betaine (XXXIII):

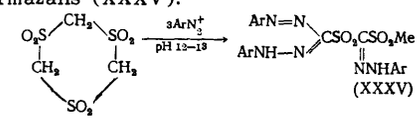
$$(XXXI) \xrightarrow{p\text{-}NO_2C_6H_4N_2^+BF_4^-} \left[(PhSO_2)_2C{=}NNC_6H_4NO_2\text{-}p \ \big| \ N{=}NC_6H_4NO_2\text{-}p\right] \rightarrow (XXXIII) + 2PhSO_2^- \ (XXXIV);$$
$$PhSO_2^- + p\text{-}NO_2C_6H_4N_2^+BF_4^- \rightarrow (XXXII) .$$

Subsequently it was shown that aromatic DS form hydrazones in an alkaline medium (pH 8–13) in the presence of an equimolar reactant ratio, while the betaines (XXXIII) are formed under the same conditions when the reaction is carried out with a twofold excess of the diazonium salt containing electron-accepting substituents in the *p*- or *m*-position in the aromatic ring.[12,28,148,160,161] Aliphatic DS are more reactive in this reaction. The interaction of bis(ethanesulphonyl)methane with diazonium salts terminates at the hydrazone stage only when *o*-substituted salts are employed, while *m*- and *p*-substituted salts in both strongly alkaline (pH 11) and weakly alkaline (pH 8.2) media react with formation of betaines (XXXIII).[162] The reactions of arenesulphonyltrifluoromethanesulphonylmethanes with diazonium salts in a weakly alkaline medium (pH 8.3) lead to the formation of hydrazones.[30]

Trimethylenetrisulphone (TTS) reacts with diazonium salts in an alkaline medium (pH 9) to form the TTS trisarylhydrazone,[163] while in a neutral medium (pH 7) TTS bisarylhydrazones were obtained[164] whose structure was demonstrated by spectroscopic methods.[165]

Tris(methylmethylene)trisulphone (TMTS) gives rise to its bisarylazo-derivatives in an alkaline medium (pH 9–10).[166]

In a strongly alkaline medium (pH 12–13) TTS reacts with a threeefold excess of diazonium salts with the opening of the ring, the elimination of one $SO_2$ group, and the formation of formazans (XXXV):[167]



Disulphones with the methanesulphonyl group and electron-accepting substituents at the carbon atom of the methylidyne group (CN, COMe, COOEt) react in anhydrous

DMF,[168] in a weakly alkaline (pH 8.2) aqueous alcoholic medium,[169] or in the form of sodium salts in aqueous solution[170] with diazonium salts containing electron-accepting substituents to form arylazo-derivatives. The elimination of $MeSO_2$ and MeCO groups is not observed under these conditions:

$$ArSO_2CH(R)SO_2Me \xrightarrow{R^1C_6H_4N_2^+} ArSO_2C(R)(SO_2Me)(N{=}NC_6H_4R^1);$$
$$R = CN, COMe, COOEt;\ R^1 = o\text{-}, m\text{-}, p\text{-}Cl, Br, NO_2 .$$

Trisulphones with the methanesulphonyl group interact in an aqueous alkaline medium (pH 8–9) or in anhydrous DMF with diazonium salts containing electron-accepting substituents in the *o*- and *p*-position, forming arenediazonium trisulphonylmethanides $ArN_2^+\,\bar{C}(SO_2R)_3$. On decomposition, the latter give rise to sulphonylazo-compounds of type (XXXII) together with arylhydrazones of type (XXXI) (in DMF) or betaines of type (XXXIII) (in an aqueous alkaline medium).[170]

In their reaction with tris(fluorosulphonyl)methane in water, arenediazonium chloride exchange the anion with formation of water-insoluble arenediazonium tris(fluorosulphonyl)methanides. The decomposition of the latter on heating leads to the *aci*-forms of the aryl esters of tris(fluorosulphonyl)methane:

$$RC_6H_4N_2^+Cl^- + HC(SO_2F)_3 \xrightarrow{H_2O} RC_6H_4N_2^+C^-(SO_2F)_3 \xrightarrow[-N_2]{80-120^\circ C} RC_6H_4OS(F){=}O{=}C(SO_2F)_2;$$
(XIII)
$$R = H, p\text{-}, m\text{-}F, p\text{-}NO_2 .$$

The structure of the latter has been confirmed by chemical reactions, spectroscopic methods (IR, $^1H$ NMR, and $^{19}F$ NMR), and X-ray diffraction analysis.[171] This is the first example of the arylation of the $SO_2$ group by diazonium salts described in the literature.

(*f*) *Arylcarbamoylation and arylthiocarbamoylation.* The interaction of aromatic DS with aryl isocyanates and allyl isothiocyanates was first described in 1966.[172] The potassium salts of DS in anhydrous acetonitrile form salt-like adducts, which are converted, after acidification, into the arylamides of bis-sulphonyl-substituted acetic and thioacetic acids:[172,173]

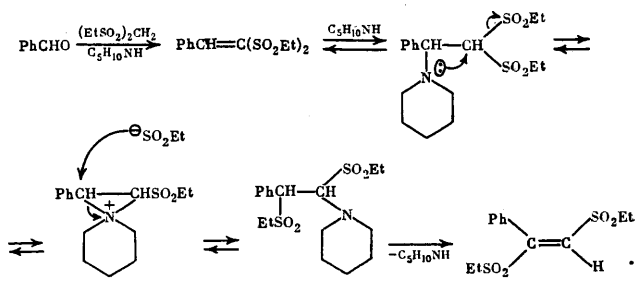
$$(ArSO_2)_2CHK \xrightarrow[MeCN,\,70-80^\circ C]{Ar^1NCX} (ArSO_2)_2CHC(XK){=}NAr^1 \xrightarrow{HCl} (ArSO_2)_2CHC(X){=}NHAr^1;$$
(XXIII)
$$X = O, S .$$

The reactions of aromatic DS with aryl isothiocyanates were later achieved in absolute alcohol in the presence of sodium ethoxide.[148,174] A novel method for the introduction of arylthio-, heteroarylthio-, and arylalkylthio-carbamoyl groups into the molecule of an aromatic DS has been developed on the basis of the reaction of active methylene groups with the methyl esters of substituted dithiocarbamic acids:[175–178]

$$RNHCSSMe + (ArSO_2)_2CH_2 \xrightarrow[EtOH]{EtONa} (ArSO_2)_2CHCSNHR;$$
$$R = Ar, 2\text{-pyridyl}, PhCH_2 .$$

This method and also the oxidative cyclisation of the arylamides of bis(arenesulphonyl)thioacetic acid by potassium hexacyanoferrate(II) in an aqueous alkaline medium[179] or by bromine in acetic acid[179] made it possible to obtain substituted heterocyclic compounds of the pyridine and benzothiazole series containing GSG in the side chain.

(*g*) *Interaction with aldehydes.* The pyridine-catalysed condensation of bis(ethanesulphonyl)methane with benzaldehyde is accompanied by a stereospecific intermolecular rearrangement with formation of *E*-αβ-bis(ethanesulphonyl)styrene [62] instead of the expected ββ-bis(ethanesulphonyl)styrene, the formation of which in this reaction had been erroneously reported earlier:[180,181]



As mentioned above (Section II), aromatic DS react with aldehydes to form 1,1,2-trisubstituted ethylenes; the interaction with aliphatic aldehydes is then frequently accompanied by the isomerisation of the final product owing to the prototropic allylic rearrangement.[60] In the condensation of bis(benzenesulphonyl)methane with isobutyraldehyde, the yields of the normal and isomerised reaction products were the same.[182] The condensation with other aliphatic aldehydes affords only isomerisation products:[182]

$$(PhSO_2)_2CH_2 \xrightarrow{\text{iso-PrCHO}} (PhSO_2)_2C{=}CHPr\text{-iso} + (PhSO_2)_2CHCH{=}CMe_2$$
$$50\% \qquad 50\%$$
$$\xrightarrow{RCH_2CHO} (PhSO_2)_2CHCH{=}CHR;$$
$$R = Et, Pr .$$

The reaction of DS with furfural yields the expected products—furfurylidenebis(sulphonyl)methanes, but under these conditions bis(benzenesulphonyl)methane and butyraldehyde react to form only the isomerisation product—1,1-bis(benzenesulphonyl)pent-2-ene.[183] Methanedisulphonyl fluoride reacts with *p*-dimethylaminobenzaldehyde in acetic anhydride to form ββ-difluorosulphonyl)-*p*-dimethylaminostyrene.[33] The condensation of DS with formaldehyde in the presence of bases leads to asymmetrically substituted propane with GSG at the terminal carbon atom.[55,57–59] Only the use of a large excess of piperidine and pyrrolidine makes it possible to carry out the Mannich reaction involving DS and to isolate the corresponding bases:[60,61]

$$(I) + CH_2O + HN\langle\rangle \rightarrow (RSO_2)_2CHCH_2N\langle\rangle$$

(*h*) *Reactions with mercury salts.* Organomercury compounds and mercury salts react with DS as electrophiles. Bis(benzenesulphonyl)methane and 1,1-bis(benzenesulphonyl)ethane reacts with *p*-dimethylaminophenylmercury hydroxide to form mercury derivatives of DS which are resistant to spontaneous disproportionation:[184]

$$p\text{-}Me_2NC_6H_4HgOH + (PhSO_2)_2CH_2 \rightarrow (PhSO_2)_2CHHgC_6H_4NMe_2\text{-}p .$$

The interaction with bis(arenesulphonyl)methanes with mercury diacetate affords mono- and di-mercurated products depending on the conditions:[185]

$$(p\text{-}RC_6H_4SO_2)_2CH_2 \xrightarrow{Hg(Ac)_2} \begin{cases} \rightarrow (p\text{-}RC_6H_4SO_2)_2CHHgAc; \\ \quad (XXXVI) \\ \rightarrow (p\text{-}RC_6H_4SO_2)_2C(HgAc)_2; \end{cases}$$
$$R = H, Me, Cl, NO_2 .$$

Bis(arenesulphonyl)methylmercury halides are formed when the potassium salts of bis(arenesulphonyl)methanes or mercuriacetates (XXXVI) interact with mercury or potassium halides respectively:

$$(p\text{-}RC_6H_4SO_2)_2CHK \xrightarrow{HgX_2} (p\text{-}RC_6H_4SO_2)_2CHHgX\ ;$$
$$(XXXVI) \xrightarrow{KX} (XXXVII)$$
$$R=H, Me;\ X=Cl, Br, I\ .$$

The C–H bond in the series of DS is readily cleared by nucleophiles ($Na_2S$) but is comparatively resistant to attack by electrophiles: only prolonged reaction with bromine or hydrogen chloride leads to its cleavage.[185]

The study of the chemical properties and IR spectra of mercurated derivatives[185] established that the C–Hg bond is covalent, is appreciably polarised, and its character is close to that of the C–Br bond in the mono- and di-bromo-derivatives of DS.

(*i*) *Reactions with formation of ylides.* Disulphones are capable of acid-base interactions with phosphines. Tertiary phosphines react with fluorinated DS to form tertiary phosphonium salts. As a result of protonation at the nitrogen atom, aminophosphines form salts which are then converted into the dialkylammonium salts of α-phosphino-substituted DS (XXXVIII):[186]

$$RSO_2CH_2SO_2CF_3 \xrightarrow{R^1_3P} R^1_3P{-}{-}{-}HCH(SO_2R)(SO_2CF_3) \rightleftarrows R^1_3\overset{+}{P}H\ \bar{C}H(SO_2R)(SO_2CF_3)\ ;$$
$$RSO_2CH_2SO_2CF_3 \xrightarrow{R^2_2PNEt_2} R^2_2\overset{+}{P}NHEt_2\ \bar{C}H(SO_2R)(SO_2CF_3) \longrightarrow$$
$$\longrightarrow R^2_2PCH(SO_2R)SO_2CF_3 + HNEt_2 \longrightarrow \underset{(XXXVIII)}{R^2_2P\bar{C}(SO_2R)SO_2CF_3\ H_2\overset{+}{N}Et_2}\ ;$$
$$R=Ph, CF_3;\ R^1=Et;\ R^2=Ph\ .$$

The salts (XXXVIII) are alkylated (with transfer of the reaction centre) at the phosphorus atom with formation of phosphorus ylides.[186]

Halogenophosphoranes react with aromatic DS in the presence of triethylamine to form phosphonium ylides with the halogen atom at the phosphorus atom—*P*-halogenoylides (XXXIX):[187]

$$Ph_nPHal_{5-n} + CH_2(SO_2Ph)_2 \xrightarrow{2NEt_3} \underset{(XXXIX)}{Ph_nPHal_{3-n}{=}C(SO_2Ph)_2}\ ;$$
$$n=2, 4;\ Hal=Cl, Br\ .$$

*P*-Halogenoylides (XXXIX) have also been obtained by treating with carbon tetrahalides the products of the reaction of tervalent phosphorus halides with bis(benzenesulphonyl)methane:[188,189]

$$R_2PCl + CH_2(SO_2Ph)_2 \xrightarrow{NEt_3} R_2P{-}CH(SO_2Ph)_2 \xrightarrow{CHal_4}$$
$$\rightarrow \underset{Hal\ \ldots\ CHal_3}{R_2\overset{\delta+}{P}{-}CH(SO_2Ph)_2} \rightarrow \underset{(XXXIX)}{R_2P(Hal){=}C(SO_2Ph)_2} + CHHal_3\ .$$

Another method of synthesis of the ylides (XXXIX) involves the interaction of chloro- or bromo-bis(benzenesulphonyl)-methanes with chlorodiphenylphosphine in the presence of triethylamine.[190] *P*-Halogenoylides with GSG virtually lack basicity. They do not interact with hydrogen chloride and do not enter into the Wittig reaction with carbonyl compounds. The halogen atom in the ylides (XXXIX) readily undergoes nucleophilic substitution:

$$(XXXIX) \xrightarrow{R^1ONa} \underset{R^1=Me, Ph}{R_2P(OR^1){=}C(SO_2Ph)_2}\ ;$$
$$(XXXIX) \xrightarrow[Et_3N]{H_2O} \underset{(XL)}{R_2P(O)CH(SO_2Ph)_2}\ ;$$
$$(XXXIX) \xrightarrow{2RR^1NH} \underset{R=R^1=H, Alk;\ R=H, R^1=Alk}{R_2P(NR^1_2){=}C(SO_2Ph)_2}\ ;$$
$$(XXXIX) \xrightarrow[Et_3N]{EtSH} R_2P(SEt){=}C(SO_2Ph)_2\ .$$

The strong electron-accepting effect of the two benzenesulphonyl groups in the phosphine oxide (XL) determines the high acidity of the compound ($pK_a = 3.27$ in 95% alcohol), as a result of which reactions involving the oxygen of the phosphoryl group are typical of this compound.[191] The same effect is responsible for the occurrence of the phosphine oxide–hydroxy-ylide tautomerism of these compounds and for the possibility of the existence of phosphonium ylides with the OH group at the phosphorus atom:[192]

$$(XL) \xrightarrow{CH_2N_2(MeI)} Ph_2P(OMe){=}C(SO_2Ph)_2\ ;$$
$$Ph_2\underset{\underset{O}{\|}}{P}{-}CH(SO_2C_6H_4P\text{-}p)_2 \rightleftarrows Ph_2P{=}\underset{\underset{OH}{|}}{C}(SO_2C_6H_4R\text{-}p)_2\ ;$$
$$R=Cl, H, Me, MeO\ .$$

The stable dimethylsulphonium di(fluorosulphonyl)-methylide has been obtained from methanedisulphonyl fluoride in DMSO in the presence of acetic anhydride.[33] When compound (VII) is acted upon by diacetoxyiodobenzene or the corresponding *m*-nitro-derivative, iodine ylides are formed:[33]

$$\underset{(VII)}{CH_2(SO_2F)_2} \xrightarrow[Ac_2O,\ 12\ h,\ 20\ ^\circ C]{Me_2S{=}O} Me_2S{=}C(SO_2F)_2\ ;$$
$$\underset{(VII)}{CH_2(SO_2F)_2} \xrightarrow{RC_6H_4I(OAc)_2} RC_6H_4I{=}C(SO_2F)_2\ ;$$
$$R=H, m\text{-}NO_2$$

(*j*) *Other reactions.* α-Diazo-β-disulphones (XLI) have been obtained by the interaction of tosyl azide with DS in an aqueous alcoholic medium in the presence of a base:[193]

$$(I) \xrightarrow[NaOH]{TsN_3} \underset{(XLI)}{(RSO_2)_2CN_2}\ ;$$
$$R=Ph, 2,4\text{-}Me_2C_6H_3, 2,4,6\text{-}Me_3C_6H_2\ .$$

The coupling reaction between compounds (XLI) and the carbanions of CH acids proceeds with elimination of one arenesulphonyl group.[193] Thermal decomposition of compounds (XLI) and its mechanism have been investigated.[193,194]

Bis(methanesulphonyl)nitromethane reacts with diazomethane to form the *N*-oxide (XLII) and the reaction proceeds via oxathiazole oxide as an intermediate:[119]

$$(MeSO_2)CHNO_2 \xrightarrow{CH_2N_2} (MeSO_2)_2CH{-}\overset{\overset{O}{\uparrow}}{N}{-}{-}O{-}N \xrightarrow{-N_2} \underset{(XLII)}{(MeSO_2)_2CH{-}N\!\!<^{CH_2}_{O}}\ .$$

The final product (XLII) is readily converted to isonitroso-bis(methanesulphonyl)methane (XLIII):

$$(XLII) \xrightarrow[-CH_2O]{H_2O} (MeSO_2)_2CHNO \rightleftarrows \underset{(XLIII)}{(MeSO_2)_2C{=}NOH}\ .$$

The isonitroso-compounds (XLIII) form salts with piperidine and hydrazine and are readily alkylated by dimethyl sulphate and acylated by acetic anhydride with formation of bis-(methanesulphonyl)-methoxyiminomethane or -acetoxyimino-methane.[119] Compound (XLIII) is unstable and it has been suggested that it decomposes via a radical mechanism.[195] On reaction of the isonitrosomethane (XLIII) with diazomethane under anhydrous conditions, 1-hydroxy-2,2-bis-(methanesulphonyl)aziridine was isolated:[196]

$$(XLIII) \xrightarrow[-N_2]{CH_2N_2} (MeSO_2)_2C{-}NOH\ (\text{with } CH_2 \text{ bridge})\ .$$

The synthesis and oxidation of *NN*-bis(arenesulphonyl)-hydroxylamines have been described.[197]

The possibility of using the thiosulphonates $(RSO_2)_2.CHSSO_2R$ for the sulphenylation of aliphatic ketones and other compounds with an active methylene group in an alkaline medium has been reported.[198]

## 2. Chemical Properties of Unsaturated GS

(*a*) *1,1-Bis(arenesulphonyl)ethylenes.* The strong polarisation of the double bonds in 1,1-bis(arenesulphonyl)-ethylenes, caused by the overall electron-accepting effect of the two sulphonyl groups, lowers appreciably the π-electron density at the β-carbon atom, which facilitates the attack by the nucleophile and makes nucleophilic addition reaction characteristic of the given series of compounds. Highly basic nucleophiles promote (particularly in protic media) the competing double bond dissociation reaction. These factors are responsible for the wide variety of the chemical properties of 1,1-bis(arenesulphonyl)ethylenes.

The acid- and base-catalysed addition of water to 1,1-bis-(arenesulphonyl)ethylenes [57] does in fact lead to the formation of 1,1,3,3-tetrakis(arenesulphonyl)propanes (XVII).[57–60,199] A mechanism has been proposed for this reaction:[57]

$$\underset{\text{(XVIII)}}{(RSO_2)_2C{=}CH_2} \underset{}{\overset{H_2O}{\rightleftarrows}} \underset{\text{(C)}}{(RSO_2)_2CHCH_2OH} \rightleftarrows \underset{\text{(D)}}{(RSO_2)_2\bar{C}H} + CH_2O + H^+ ;$$

$$\text{(C)} \overset{H^+}{\rightleftarrows} (RSO_2)_2\overset{+}{C}HCH_2\overset{+}{O}H_2 \xrightarrow[-H_2O]{(D)} \underset{\text{(XVII)}}{[(RSO_2)_2CH]_2CH_2} ;$$

R = Ar .

The C–C bond in compounds (C) is appreciably polarised under the influence of the two arenesulphonyl groups and is capable of hydrolytic cleavage by bases or acids. The formation of the carbanion (D) is apparently the rate-limiting stage in the overall reaction. The final products can be formed both via the pathway indicated in the scheme and via the interaction of the initial olefin with the anion (D). In ahydrous $CCl_4$ the olefin (XVIII) combines with aromatic and heterocyclic thiols, while in the presence of acetic acid it can combine with sulphinates.[57] They are active acceptors in the Michael reaction and in the presence of $F^-$ they readily combine with DS, TS, nitromethane, and arenesulphonylacetonitrile.[57] It has been shown that the reactions of the olefin (XVIII) with TS are also catalysed by a Lewis acid ($BF_3$ etherate),[56] while the interaction with β-diketones (acetylacetone and dibenzoylmethane) proceeds in dioxan in the presence of Triton B (200). ββ-Bis(benzenesulphonyl)styrene combines with malonic ester.[64] The use of 1,1-bis(benzenesulphonyl)ethylene as the dienophile in cycloaddition reactions with cyclopentadiene, cyclohexa-1,3-diene, cycloheptatriene, and other dienes has been described recently.[61] The study of the reactions of 1,1-bis(benzenesulphonyl)ethylene with various amines showed that, depending on the basicity of the amine, the reaction proceeds via two pathways: with formation of adducts (XLIV) or substituted propanes (XVII):[199]

$$(PhSO_2)_2C{=}CH_2 \begin{cases} \xrightarrow{\text{amines } (pK_a\ 1.0\text{–}6.9)} \underset{\text{(XLIV)}}{(PhSO_2)_2CHCH_2NHR} ; \\ \xrightarrow{\text{amines } pK_a\ 9.3\text{–}11.2)} \underset{\text{(XVII)}}{} . \end{cases}$$

A mechanism has been proposed[199] for the reaction of 1,1-bis(benzenesulphonyl)ethylene with highly basic amines:

$$\underset{\text{(XVIII)}}{(PhSO_2)_2C{=}CH_2} \xrightarrow{RNH_2} \text{(XLIV)} \rightleftarrows$$

$$\rightleftarrows (PhSO_2)_2\bar{C}H + [CH_2 \cdots NHR]^+ \xrightarrow{RNH_2} CH_2(NHR)_2$$
$$\downarrow (PhSO_2)_2C{=}CH_2 \qquad (PhSO_2)_2\bar{C}H \downarrow$$
$$(PhSO_2)_2\bar{C}CH_2CH(SO_2Ph)_2 \xrightarrow{H^+} \text{(XVII)} .$$

The rate of heterolysis of the C–C bond in the amine (XLIV) exceed the rate of its formation, as a result of which the DS carbanion can react with both the initial olefin and with the second heterolysis product—the aminal (the nitrogen-containing derivative of formaldehyde), to form the propanes (XVII). The olefins (XVIII) interact with electrophiles only with difficulty. They combine with bromine in acetic acid on heating. Mercury acetate undergoes the Hofmann–Sand reaction with two ethylene molecules and the addition takes place contrary to the Markovnikov rule:[57]

$$(PhSO_2)_2C{=}CH_2 \xrightarrow{Hg(OAc)_2MeOH} [MeOCH_2C(SO_2Ph)_2]_2Hg .$$

ββ-Bis(benzenesulphonyl)styrene reacts with diazomethane to give a substituted pyrazoline, which is converted into 1,1-bis(benzenesulphonyl)-3-phenylprop-3-ene on heating:[64]

$$(PhSO_2)_2C{=}CHPh \xrightarrow{CH_2N_2} (PhSO_2)_2C(\text{—}N{=}N\text{—}CH_2\text{—})CHPh \rightarrow (PhSO_2)_2CHCH{=}CHPh .$$

A thermal stereospecific rearrangement catalysed by ammonium salts has been discovered for the olefins (XVIII). On heating (138–139 °C) in *p*- or *m*-xylene in the presence of catalytic amounts of ammonium salts, the *gem*-substituted olefins (XVIII) rearrange to *E*-1,2-bis(arenesulphonyl)-ethylenes:[201]

$$\text{(XVIII)} \xrightarrow[\text{ammonium salts}]{\Delta} p\text{-}RC_6H_4SO_2\text{—}C(H){=}C(H)\text{—}SO_2C_6H_4R\text{-}p ;$$

R = H, Me, Cl .

A rearrangement in the opposite direction has been observed in the nucleophilic vinyl substitution reaction when 1,2-bis-[alkane(or arene)sulphonyl]-1,2-dichloroethylenes are treated with amines:[202]

$$RSO_2C(Cl){=}C(Cl)SO_2R \xrightarrow{R^1NH_2} (RSO_2)_2C{=}C(NR^1)_2 ;$$

$R = Et, C_8H_{17}, Ph; R^1 = Ph, p\text{-}HOC_6H_4, p\text{-}NO_2C_6H_4$ .

(*b*) *Polysulphonylethylenes.* The presence of four electron-accepting groups in the molecules of tetrasulphonylethylenes (TSE) (XLV) entails a high reactivity of these compounds. In aqueous solutions the TSE are hydrolysed with dissociation of the C=C bond[203] and the formation of disulphonylmethanes. This process proceeds readily in neutral, acid, and basic media. The mechanism of the hydrolysis of TSE [203] is based on a detailed study of the kinetics of the hydrolytic reactions of asymmetric olefins activated by several electron-accepting groups:[204,205]

$$(RSO_2)_2C{=}C(SO_2R)_2 \underset{}{\overset{H_2O}{\rightleftarrows}} (RSO_2)_2C(OH)\text{—}\bar{C}(SO_2R)_2 \overset{H^+}{\rightleftarrows}$$

$$\rightleftarrows (RSO_2)_2C(OH)CH(SO_2R_2) \rightarrow \text{(I)} + [(RSO_2)_2C{=}O] \xrightarrow{H_2O_2} RSO_3H + CO_2 ;$$

R = Et, *n*-Bu .

The extremely ready fragmentation of TSE is the reason why their synthesis is possible only under anhydrous conditions.[74] Alcohols which react readily with TSE do not form fragmentation products. In the presence of urea, the reactions of TSE with alcohols lead to the esters of bis(alkanesulphonyl)acetic acids:[203]

$$\text{(XLV)} \xrightarrow{R^1OH} [(RSO_2)_2C{=}C(OR^1)SO_2R] \xrightarrow{R^1OH} (RSO_2)_2C{=}C(OR^1)_2 + 2RSO_3H ;$$
$$\downarrow H_2O \qquad\qquad (RSO_2)_2CHCOOR^1 \xleftarrow{H_2O} \downarrow$$

$R = Et, R^1 = Me, Et$ .

The ideas concerning the course of the interaction of TSE with alcohols have been confirmed by a study of the reactions of TSE with thiols, where the intermediate thioacetals and their dioxides proved to be stable:[203]

$$(XLV) \xrightarrow{R^1SH} (RSO_2)_2C{=}C(SO_2R)(SR^1) + (RSO_2)_2C{=}C(SR^1)_2 ;$$
(XLVI)
R = Et, *n*-Bu, $R^1$ = Et, Ph .

Thioacetal *SS*-dioxides readily hydrolyse with the elimination of the $SO_2R$ group:

$$(XLVI) \xrightarrow{H_2O} (RSO_2)_2CHCOSR^1 \rightleftarrows (RSO_2)_2C{=}C(OH)SR^1$$
(XLVII) (XLVIII) .

According to IR spectroscopic data, the hydrolysis products exist both in the form of the esters (XLVII, R = n-Bu, $R^1$ = Et) and in the enolic form (XLIII, R = Et, $R^1$ = Ph).

The reactions of TSE with secondary or bulky primary amines take place with formation of bis(sulphonyl)acetamides—the products of the hydrolysis of the unstable 1,1,2-tris-(sulphonyl)-2-(R-amino)methylenes.[206] A mechanism has been proposed for the reactions with amines on the basis of the $Ad_N - E$ nucleophilic substitution mechanism for other electrophilic olefins.[207,208]

Together with the formation of disulphonylacetamides, primary amines give rise to the formation in this reaction of 1,1-bis[alkane(or arene)sulphonyl]-2,2-bis[alkyl(or aryl)amino]ethylenes—the products of the substitution of two sulphonyl groups.[206] Fragmentation has been observed only when highly basic amines were employed, bis-sulphonyl)methanes being apparently formed as a result of the competitive cleavage of the TSE by the amines.

(c) *2,2-Bis(alkanesulphonyl)- and 2,2-bis(arenesulphonyl)-vinyl ethyl ethers.* The different electronic natures of the substituents at C(1) and C(2) in these compounds are responsible for their unusual chemical behaviour. In contrast to unsubstituted ethyl vinyl ethers, 2,2-bis-(sulphonyl)vinyl ethers (VE) do not react with alcohols and do not form acylals on reaction with acetic acid. Addition reactions are not characteristic of these compounds. 2,2-Bis(benzenesulphonyl)vinyl ethyl ether forms a complex mixture of products on heating with bromine in $CCl_4$, from which bis(benzenesulphonyl)bromomethane was isolated (10%).[65] Like TSE, the VE hydrolyse in acid and alkaline media with rupture of the double bond and the formation of bis(arenesulphonyl)methanes.[65] VE react with ammonia to form 2,2-bis[alkane(or arene)sulphonyl]-vinylamines.[62,64,65] The latter are acylated by benzoyl chloride, react with ethyl and phenyl isocyanates to form substituted ureas, react with tosyl chloride (in the presence of BuLi),[62,65] and are reduced by sodium tetrahydroborate to 1,1-bis(alkanesulphonyl)- or 1,1-bis(arenesulphonyl)-ethanes.[58]

2,2-Bis(arenesulphonyl)vinylamines have also been synthesised from the sodium salts of bis(arenesulphonyl)-methanes, DMF, and dimethyl sulphate[58] or by the reaction of bis(arenesulphonyl)methanes with bis(trimethylsilyl)-formamide:[209]

$$(p\text{-}RC_6H_4SO_2)_2CH_2 \xrightarrow[HCON(SiMe_3)_2,\ 120°-140°C]{Me_2SO_4DMF} (p\text{-}RC_6H_4SO_2)_2C{=}CHNH_2 ;$$
R=H, $CH_3$, Cl .

2,2-Bis(toluene-*p*-sulphonyl)vinylamine reacts with phenyl isothiocyanate in the presence of triethylamine to form *N*-[2,2-bis(toluene-*p*-sulphonyl)vinyl]aniline and not a substituted thiourea as was expected:[210]

$$(p\text{-}MeC_6H_4SO_2)_2C{=}CHNH_2 \xrightarrow[Et_3N,120-140°C]{PhNCS} [(p\text{-}MeC_6H_4SO_2)_2C{=}CHNHCSNHPh] \xrightarrow{Et_3N} \rightarrow (p\text{-}MeC_6H_4SO_2)_2C{=}CHNHPh + (Et_3NH)^+SCN^- .$$

Ethyl vinyl ethers containing alkanesulphonyl groups (XLIX) react with aromatic[130] and aliphatic (primary and secondary) amines[62] in the presence of TsOH to form substituted vinylamines:

$$(RSO_2)_2C{=}CHOEt \xrightarrow[TsOH]{R^1R^2NH} (RSO_2)_2C{=}CHNR^1R^2 ;$$
(XLIX)
R = Me, Et; $R^1$ = Ph, $R^2$ = H or $R^1$, $R^2$ = Alk .

The same reaction of VE containing arenesulphonyl groups is accompanied by a competing process—the dissociation of the double bond, which greatly reduces the yield of the required products.[65] Ethyl vinyl ethers (L) react with dihydroresorcinol,[64] 2,4-dinitrophenylhydrazine,[65] and hydroxylamine[62] to form substitution products. Alkaline hydrolysis of the VE (L) at the interface between two phases leads to acetaldehyde with GSG:[64]

$$(ArSO_2)_2C{=}CHOEt \xrightarrow[CHCl_3]{KOH} (ArSO_2)_2CHCHO ;$$
(L)
Ar = Ph .

Nucleophilic substitution of the OEt group in the VE (L) by the carbanions of CH acids results in the formation of 1,1,3,3-tetrasubstituted propenes:[64,75]

$$(ArSO_2)_2C{=}CHOEt \xrightarrow[EtONa/EtOH]{R^1CH_2COOEt} (ArSO_2)_2C{=}CHCH(R^1)COOEt ;$$
$R^1$ = COMe, CN.

(d) *Polysulphonylpropenes.* Propenes with GSG at C(1) or C(3), containing simultaneously two other electron-accepting substituents at the terminal carbon atoms [C(3) and C(1) respectively] have been described.[64,75,76] In solution these compounds are involved in a tautomeric equilibrium:[75,76]

$$R^1R^2C{=}CHCHR^3R^4 \rightleftarrows R^1R^2CHCH{=}CR^3R^4 ,$$
(LI) : $R^1$=$R^2$=$PhSO_2$; $R^3$ = COMe; $R^4$ = COOEt ;
(LII) : $R^1$=$ArSO_2$; $R^2$=CN; $R^3$=$R^4$=$SO_2Et$, $SO_2Ar$ .

The chemical reactions of propenes with GSG are determined mainly by their CH-acid properties (Table 4). The propenes (LII) form salts with alkali metals, react with diazonium salts and bromine, and form products resulting from the substitution of the hydrogen atom at C(1).[76] The propenes (LII, $R^3$ = $R^4$ = $SO_2Ar$) are nitrated with dissociation of the double bond and the formation of bis(4-R-3-nitrobenzene-sulphonyl)methanes.[27] The propene (LI) reacts with diazonium salts to form the product of substitution at C(3),[211] the nitration of compound (LI) is accompanied by the rupture of the double bond and leads to bis(3-nitro-benzenesulphonyl)methane, and nitrosation affords ethyl γγ-bis(benzenesulphonyl)-α-hydroxyiminovinylacetate:[27]

$$(LI) \xrightarrow[pH\ 8,3]{R^1C_6H_4N_2^+} (PhSO_2)_2C{=}CHC(N{=}NC_6H_4R^1)(COMe)COOEt ;$$
$$(LI) \xrightarrow{HNO_3,H_2SO_4} (3\text{-}O_2NC_6H_4SO_2)_2CH_2 ;$$
$$(LI) \xrightarrow{NaNO_2,HAc} (PhSO_2)_2C{=}CHC(COOEt){=}NOH ;$$
$R^1$ = *p*-Cl, *p*-Br, *m*-$NO_2$.

1,1-Bis(benzenesulphonyl)-2-cyano-2-ethoxycarbonylprop-1-ene, which has a similar structure but is much more acid ($pE_a$ = 1.04 in acetone), reacts with diazonium salts in the tautomeric prop-3-ene form with substitution of the hydrogen atom at C(1), the elimination of the EtOCOC(CN) =CH group, and the formation of 1,3-diaryl-5-hydroxytetrazolium betaines (XXXIII).[211]

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Thus GS exhibit a varied reactivity. Further investigation of the chemistry of compounds of this class will lead to the discovery of their new practical applications as physiologically active preparations,[212] pesticides,[213] and in the manufacture of polymeric materials.[214–222]

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# Non-traditional Oxidants in Preparative Coordination Chemistry

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The application of nitrosonium and arenediazonium salts, carbenium, silver(I), and mercury(II) ions, protic acids, and amine oxides as oxidants in preparative coordination chemistry is examined. Specific examples illustrate which problems in the field of the synthesis and reactions of coordination compounds can be solved with the aid of these oxidants.
The bibliography includes 158 references.

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## I. INTRODUCTION

Many synthetic methods are based on the use of oxidants in preparative coordination chemistry, among which oxidants, one may include the halogens, oxygen, hydrogen peroxide, concentrated nitric acid, permanganates, bromates, persulphates, etc. The choice of oxidants depends on the problem to be solved. It is sometimes required to oxidise the central atom of a complex without affecting the ligand, while in other cases it is necessary to oxidise the ligand without affecting the central atom. The products of the reduction of oxidants are frequently themselves ligands, which is sometimes a decisive factor in the choice of the oxidant. The larger the set of oxidants available to the synthetic chemist, the easier it is to solve specific problems.

In the last 10–15 years the range of oxidants in coordination chemistry has been greatly expanded by the use of non-aqueous solvents. The solvent as a rule influences strongly the oxidation-reduction potential of the system. One of the causes of this behaviour is the different degrees of solvation of the oxidant molecule and its reduction products. For example, the high oxidation potential of chlorine in polar solvents is associated, in particular, with the much higher solvation energy of two chloride ions than that of the $Cl_2$ molecule, which tends to shift the equilibrium to the right in the presence of the solvent. In [weakly] solvating solvents the difference between the solvation energies of the chlorine molecule and chloride ions is smaller and this is reflected in a decrease of the oxidation potential. In practice this amounts to the observation

that chlorine becomes a milder oxidant in a weakly solvating solvent. Thus, attempts[1] to obtain platinum(IV) complexes of hydroxylamine by oxidising $[Pt(NH_2OH)_2X_2]$ (X = Cl or Br) by halogens in an aqueous solution led to the decomposition of the coordinated $NH_2OH$ molecule and the formation of acido- and hydroxo-complexes of platinum(IV). When this reaction was carried out in the weakly solvating $CCl_4$, the corresponding platinum(IV) complexes with coordinated hydroxylamine were obtained.

In recent years oxidants which may be referred to as non-traditional have been introduced into preparative chemistry to an increasing extent. The term "new oxidants" would not be altogether accurate since individual instances of their use have been known for a fairly long time. The fact that the oxidants considered in this review are sometimes fairly specific in the oxidation of particular ligands in coordination compounds is of special interest to synthetic chemists. They make it possible to direct the oxidation process to a specific site in the complex.

## II. NITROSONIUM SALTS

Nitrosonium salts are one-electron oxidants which have been most frequently used during the last decade. According to Mussini[2] and Schmid and Neumann,[3] the redox potential of the $NO^+/NO$ pair in aqueous solution is 1.45 V (1.23 V relative to the Ag/AgCl electrode). When nitrosonium salts are used in non-aqueous solvents with weak electron-donating properties, the difference between the degrees of solvation of $NO^+$ and NO diminishes and the activity in relation to oxidation reactions increases.[4] Indeed, the potential of the $NO^+/NO$ pair in nitromethane relative to the Ag/AgCl electrode is as much as 1.58 V.[5]

Various methods of preparation of the above reagents are known. Nitrosyl chloride NOCl is formed on direct interaction of $Cl_2$ and NO, in the reaction of $NOHSO_4$ or $NaNO_2$ with HCl, and also as one of the products of the reaction of KCl and $NO_2$; NOBr is usually obtained from $Br_2$ and NO.[6] In the same study a method of synthesis of nitrosyl fluoride was also described. Among the different procedures for the preparation of $NO^+BF_4^-$,[7-11] the method based on the reaction of $N_2O_3$ with aqueous $HBF_4$ solution is most often employed:[9-11]

$$N_2O_3 + 2HBF_4 \rightleftarrows 2NO^+BF_4^- + H_2O,$$

$NO^+ClO_4^-$ is obtained analogously.[11-14]

Nitrosonium salts containing large anions with a weak electron-donating capacity are used to synthesise various metal salts and homogeneous solvato-complexes. Thus, one of the first syntheses in which a nitrosonium salt was used as the oxidant was achieved in 1950:[15]

$$Na + NO^+SbCl_6^- \xrightarrow{SO_2} Na[SbCl_6] + NO.$$

Later the oxidation of metals by nitrosonium salts in electron-donating solvents came to be used in the synthesis of homogeneous solvato-complexes. Thus, the complexes $[Cu(MeCN)_4]X$ [16,17] have been obtained by oxidising copper in acetonitrile with $NO^+X^-$ (X = $BF_4$ or $ClO_4$); the perchlorate $NO^+ClO_4^-$ in MeCN is capable of oxidising metallic gold with formation of the complex $[Au(MeCN)_4](ClO_4)$.[18] The solvates $[Eu(MeCN)_n]X_3$ (X = $BF_4$ or $PF_6$),[19] $[Ni(MeCN)_6](ClO_4)_2$,[20] and $[Pd(MeCN)_4](BF_4)_2$ [21,22] have been synthesised by oxidising metals with nitrosonium salts.

The oxidation of the complex $[Re_2Cl_4(PMe_2Ph)_4]$ with metal–metal bonds by one mole of $NO^+PF_6^-$ in acetonitrile led to the formation of $[Re_2Cl_4(PMe_2Ph)_4](PF_6)$ in 73% yield. The complex $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$ has been isolated in 90% yield as a result of the interaction of the initial compound with 3.5 moles of $NO^+PF_6^-$.[23]

The oxidation of the complexes $[Cr(NO)(CNCMe_3)_4(PR_3)]X$, where R = Et or Bu, by $NO^+X^-$ salts (X = $BF_4$ or $PF_6$) in acetone is completed after 10 min with the formation of the products $[Cr(NO)(CNCMe_3)_4(PR_3)]X_2$ in approximately 90% yield.[24] The reaction of the zerovalent platinum complex $[Pt(PPh_3)_2(C_2H_4)]$ with nitrosonium tetrafluoroborate in acetonitrile led to the oxidation of the central atom with the simultaneous substitution of the coordinated ethylene by solvent molecules:[25]

$$[Pt(PPh_3)_2(C_2H_4)] + 2NO^+BF_4^- + 2MeCN \rightarrow$$
$$\rightarrow [Pt(PPh_3)_2(MeCN)_2](BF_4)_2 + C_2H_4 + 2NO.$$

The oxidation of the complex $MoL(NO)(CO)_2$ [L = tris(3,5-dimethylpyrazolyl)borate] by nitrosyl chloride is accompanied by substitution of the coordinated carbonyl groups by chloride ions:[26]

$$MoL(NO)(CO)_2 + 2NOCl \xrightarrow{CH_2Cl_2} MoL(NO)Cl_2 + 2CO + 2NO.$$

In the above examples the substitution of the ligands by the nitrosyl group was not noted. However, a series of studies have produced data indicating a dual reactivity of nitrosonium salts towards metal complexes. It has been established that the $NO^+$ cation can react to give either the corresponding nitrosyl derivatives or oxidation products. Sometimes both processes take place simultaneously. It has been shown[27,28] that the product of the reaction of $Mo(CO)_6$ with $NO^+$ in acetonitrile may be different under different experimental conditions. Thus, when the NO formed in the reaction is removed from the reaction mixture, the complex $[Mo(NO)(MeCN)_5]^{2+}$ is obtained, whereas, in the case where the reaction is carried out in the presence of NO, $[Mo(NO)_2(MeCN)_4]^{2+}$ is isolated. When these investigations were continued, it was established[29] that, when the reaction between $[Cr(CO)_4L]$ [L = bis(diphenylphosphino)-methane (Dppm) or 1,2-bis(diphenylphosphino)ethane (Dppe)] and $NO^+BF_4^-$ in $CH_2Cl_2$ is carried out in a closed nitrogen-filled flask, the product is the complex $[Cr(CO)_3(NO)L]^+$. On the other hand, when NO is removed from the reaction sphere by bubbling nitrogen through the reaction mixture, the oxidation product $[Cr(CO)_4L]^+$ is formed. The studies carried out by Connelly's group led to the mechanism

$$[ML_n] + NO^+ \rightarrow [ML_n(NO)]^+ \begin{cases} \rightarrow [ML_n]^+ + NO; \\ \rightarrow [ML_{n-1}(NO)]^+ + L. \end{cases}$$

The mechanism illustrates the fact that a change in reaction conditions can shift the equilibrium and can lead to the possibility of obtaining either the oxidation product $[ML_n]^+$ or the substituted nitrosyl complex $[ML_{n-1}(NO)]^+$. The latter can also be regarded as the oxidation product when the coordinated nitrosyl is converted into the $NO^-$ anion. It has been stressed[29] that the nature of the central atom M and of the coordinated ligand L can appreciably affect the equilibrium position. The ability of the complex $[ML_n]$ to form intermediates of the type $[ML_n(NO)]^+$ with an increased coordination number is also important.

The interaction of the complex $(Et_4N)[V(CO)_6]$ with $NO^+BF_4^-$ in dichloromethane, resulting in the formation of the substituted complex $[V(CO)_5(NO)]$ has been investigated.[30]

It has been shown that the infrared spectra of the products obtained by the interaction of $[V(CO)_6]^-$ with $NO^+$ and of $V(CO)_6$ with NO are identical. The following reaction mechanism has been proposed:[18]

$$V(CO)_6^- + NO^+ \rightarrow V(CO)_6 + NO \rightarrow [V(CO)_6(NO)] \xrightarrow{-CO} [V(CO)_5(NO)].$$

This mechanism does not conflict with Connelly's mechanism and actually supplements it.

We shall quote certain examples illustrating the dual reactivity of nitrosonium salts. When the isonitrile complex of tungsten $W(CNPh)_2$ is mixed with $NO^+PF_6^-$ in tetrahydrofuran (THF), two products are formed:[31]

$$2W(CNPh)_6 + 2NO^+PF_6^- \xrightarrow{THF} [W(NO)(CNPh)_5](PF_6) + [W(CNPh)_7](PF_6) + NO.$$

The oxidation of the osmium complex $[Os(CNR)_4X_2]$ proceeds without the formation of substitution products:[32]

$$[Os(CNR)_4X_2] + NO^+BF_4^- \xrightarrow{MeCN} [Os(CNR)_4X_2](BF_4) + NO;$$
$$R = t\text{-Bu, iso-Pr, } C_6H_{11};\ X = Cl, Br.$$

The interaction of a solution of $Mo(CO)_6$ in dichloromethane with $NO^+PF_6^-$ leads to the formation of $Mo(NO)_2(PF_6)$, which has a polymeric structure with a bridging hexafluorophosphate ligand.[33] The corresponding solvates $[Mo(NO)_2S_n].(PF_6)_2$ (S = solvent molecule) are formed from the same reactants in MeCN [34] or $MeNO_2$.[33]

It has been noted[35–38] that nitrosonium salts can react in two ways also with cluster compounds. For example, the oxidation of the anion $[Os_4H_3(CO)_{12}]^-$ by the $NO^+X^-$ salts (X = $BPh_4$ or $PF_6$) in acetonitrile gave rise to the clusters $[Os_4H_3(CO)_{12}(MeCN)_2]X$ in a yield of ~35%. The replacement of acetonitrile by dichloromethane or THF results in the formation of the compound $[Os_4H_3(CO)_{12}(NO)]$ in this reaction.[38]

It has been noted in a review[35] that nitrosyl salts are used as the source from which the nitride ligand is introduced into the carbonyl clusters of various metals.

The ability of nitrosonium salts to oxidise the coordinated azide ion is used in practice in preparative coordination chemistry:

$$[Co(NH_3)_5N_3](ClO_4)_2 + NO^+ClO_4^- \xrightarrow{S} [Co(NH_3)_5S](ClO_4)_3 + N_2O + N_2,$$

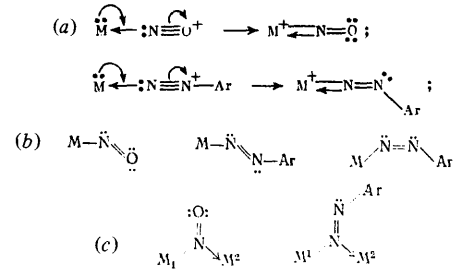
where S = tetramethylene sulphone,[39] triethyl phosphate,[40] or acetonitrile.[41,42] The reaction led to the isolation of gaseous oxidation-reduction products, the vacant site in the coordination sphere being occupied by solvent molecules.

The reaction between the phosphine complexes of nickel(II) $[Ni(PPh_3)_2X_2]$ (X = Cl, Br, or $NO_3$) and NOCl has been investigated[43,44] in a benzene–cyclohexane mixture. Without dwelling on the pathways leading to the formation of the oxidation products, the authors conclude that the reaction results in the formation of the dimers, $[Ni(OPPh_3)XCl]_2$.

## III. ARENEDIAZONIUM SALTS

The classical studies by Nesmeyanov and co-workers[45] were devoted to the oxidation and arylation of organometallic compounds, especially of ferrocene by arenediazonium salts.

Certain aspects of the coordination chemistry of arenediazonium have been examined in a review[46] and an analogy has been drawn between the nitrosyl and arenediazenate complexes of transition metals. This applies in broad outline to the valence structures of the complexes in linear (a), angular (b), and bridged (c) coordination, i.e.



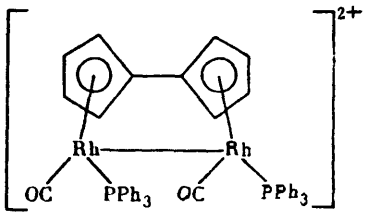
and also to the similarity of the reactivities. The analogy has been extended[29,47] to redox reactions with participation of nitrosonium and arenediazonium salts.

It has been noted[47] that there are no literature data on the oxidation potentials of nitrosonium and diazonium in any one non-aqueous solvent, i.e. under comparable conditions. However, it follows from the available potentials that $NO^+$ (1.58 V, nitromethane, Ag/AgCl electrode) is a stronger oxidant than $ArN_2^+$ (0.295 V, sulpholan, saturated calomel electrode), although strictly speaking the potentials quoted are not directly comparable. A comparative study has been made of the interaction of the complexes $[Cr(CO)_2L.(\eta\text{-}C_6Me_6)]$ [L = $PPh_3$, $PMePh_2$, $PMe_2Ph$, $P(OPh)_3$, or $P(OMe)_3$] with $NO^+PF_6^-$ and $PhN_2^+PF_6^-$ in PhMe–MeOH and $CH_2Cl_2$ respectively.[47] It has been established that nitrosonium salts give rise only to the products of substitution of CO or L, i.e. $[Cr(CO)(NO)L(\eta\text{-}C_6Me_6)](PF_6)$ and $[Cr(CO)_2(NO)(\eta\text{-}C_6Me_6)](PF_6)$. The interaction with a diazonium salt leads to the formation, together with the substitution products $[Cr(CO)(N_2Ph)L(\eta\text{-}C_6Me_6)](PF_6)$ and $[Cr(CO)_2(N_2Ph)(\eta\text{-}C_6Me_6)](PF_6)$, also of the one-electron oxidation product $[Cr(CO)_2L(\eta\text{-}C_6Me_6)](PF_6)$. In order to account for this finding, the authors[29,47] turned to the mechanism of the interaction of carbonyl complexes with nitrosonium salts which they proposed (see previous Section). On the basis of the similarity between the reactivities of $NO^+X^-$ and $ArN_2^+X^-$, they extended the scheme to the reactions of complexes of the type $[ML_n]$ with $ArN_2^+X^-$. Analysis showed, despite the more negative potential of the $ArN_2^+/ArN_2$ pair compared with that of the $NO^+/NO$ pair, diazonium salts are more reactive one-electron oxidants. On the one hand, this can be explained by the greater steric hindrance by the $ArN_2^+$ ligand to the formation of the intermediate $[ML_n(ArN_2)]^+$ and on the other, the formation of the oxidation product $[ML_n]^+$ is favoured by the irreversible formation of $N_2$ and biaryl:

$$2ArN_2^+ + 2e \rightarrow 2N_2 + Ar\text{—}Ar.$$

The oxidising capacity of diazonium salts can be used in preparative coordination chemistry. Thus the complex $[Mo(NO)(MeCN)(Dppe)_2](PF_6)$ has been oxidised by the stoichiometric amount of $[p\text{-}FC_6H_4N_2]^+(PF_6)^-$ in dichloromethane.[48] The reaction is completed in 30 min; $[Mo(NO).(MeCN)(Dppe)_2](PF_6)_2$ was isolated from the reaction mixture in 92% yield. The one-electron oxidation product $[Co(Salen)(H_2O)](BF_4)$ ($H_2Salen$ is the Schiff base prepared from one mole of ethylenediamine and two moles of salicylaldehyde) has been obtained by the reaction of [Co(Salen)] with $[p\text{-}XC_6H_4N_2]^+(BF_4)^-$ (X = H, OMe, or $NO_2$) in $CH_2Cl_2$ or $Me_2CO$ containing traces of water.[49] It has been stated[50] that diazonium salts in acetonitrile are capable of oxidising metallic copper or silver with formation of the corresponding homogeneous solvato-complexes. The oxidation can involve also coordinated ligands. Thus the interaction of $[Rh(CO)(PPh_3)(\eta\text{-}Cp)$ (Cp = cyclopentadienyl)

with $[p\text{-}FC_6H_4N_2]^+(BF_4)^-$ in dichloromethane leads to the formation of the fulvalene complex:[51]




## IV. TRIPHENYLCARBENIUM SALTS

In 1958 it was suggested[52] that triphenylcarbenium salts (the $Ph_3C^+$ cation is frequently referred to as the trityl cation in the literature) be used as powerful acceptors of hydride ions. The employment of $Ph_3C^+X^-$ in preparative coordination chemistry can be considered in terms of at least three aspects. Firstly, trityl is used as a one-electron oxidant. Secondly, it is capable of abstracting the hydride ion from an organic ligand. Thirdly, triphenylcarbenium salts are able to accept a coordinated hydride ion.

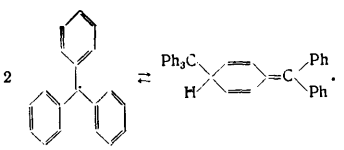
Data concerning the synthesis of triphenylmethyl perchlorate and triphenylmethyl tetrafluoroborate have been published.[53,54] The above reagents are obtained by the reaction of triphenylmethylmethanol with 71% $HClO_4$ or 48% $HBF_4$ in the presence of acetic anhydride. The latter is introduced to remove water:

$$Ph_3COH + H^+ \rightarrow Ph_3C^+ + H_2O.$$

The yields are 76 and 92% respectively. The tetrafluoroborate $Ph_3C^+BF_4^-$ has advantages over the perchlorate $Ph_3C^+ClO_4^-$ because of its greater stability.[53]

It has been established[50] that $Ph_3C^+BF_4^-$ can function as a one-electron oxidant and is able to oxidise metallic copper with formation of the homogeneous solvato-complex $[Cu(MeCN)_4](BF_4)$. The phosphine complexes of palladium(II) $[Pd(PPh_3)_4]X_2$ (X = $BF_4$ or $PF_6$) and $\{Pd[P(OPh)_3]_4\}.(PF_6)_2$ have been synthesised in 60 and 50% yields respectively by the oxidation of the complexes $[Pd(PPh_3)_4]$ and $\{Pd[P(OPh)_3]_4\}$ by the trityl cation.[55]

The triphenylmethyl radical, formed in the reduction process, dimerises with formation of 1-diphenylmethylene-4-tritylcyclohexa-2,5-diene:[56,57]




The one-electron oxidation of the complex $\{CpW(NO).[P(OMe)_3]\}$ with triphenylcarbenium tetrafluoroborate in $CH_2Cl_2$ in air led to the isolation from the reaction mixture of the already known[59] compound $Ph_3COOCPh_3$ in 13% yield.[58] Cobalt(II) complexes having the general formula $[CoHL_4]X$ [L = $P(OEt)_2Ph$, $P(OMe)_2Ph$, or $P(OPh)_3$; X = $PF_6$ or $BF_4$] have been obtained by the reaction of the corresponding hydrides $[CoHL_4]$ with a stoichiometric amount of the triphenylcarbenium salt.[60] In this case the trityl cation behaves as a one-electron oxidant and not as a hydride ion acceptor. This has been explained[60] by the greater strength of the Co–H bond.

The dependence of the reactivity of the triphenylcarbenium ion on the properties of the solvent has been clearly demonstrated in a study of the reaction of $Ph_3C^+PF_6^-$ with the polyhydride $Re_2H_8(PPh_3)_4$.[61] The abstraction of a hydride ion in acetonitrile results in the formation of a coordination-saturated intermediate, which is stabilised in the form of the solvato-complex $[Re_2H_7(PPh_3)_4(MeCN)](PF_6)$. When the reaction is carried out in dichloromethane, $Ph_3C^+PF_6^-$ functions as a one-electron oxidant, which results in the formation of $[Re_2H_8(PPh_3)_4](PF_6)$.

Other carbenium ions can be used in one-electron oxidation reactions in addition to the triphenylmethyl cation. Thus the complex $\{CpW(NO)[P(OMe)_3]\}$ is oxidised to the corresponding monocationic complex on interaction with $MeOSO_2F$ in accordance with the reaction equation

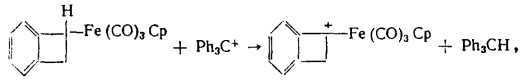
$$[CpW(NO)\{P(OMe)_3\}] + MeOSO_2F \xrightarrow{CH_2Cl_2} \rightarrow [CpW(NO)\{P(OMe)_3\}](OSO_2F) + {}^1/_2C_2H_6.$$

The ethane evolved was detected by gas–liquid chromatography (GLC).[58]

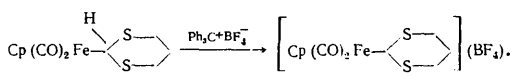
The one-electron oxidation of the complex $[MoCl_2(Dppe)_2]$ by the compound $[Et_3O]^+(BF_4)^-$ and $MeOSO_2F$ in dichloromethane leads to the formation of the molybdenum(III) complex $[MoCl_2(Dppe)_2]X$ (X = $BF_4$ or $OSO_2F$).[62] Triethyloxonium tetrafluoroborate oxidises $[Re(CO)_3Cl(PPh_3)_2]$ to the corresponding complex $[Re(CO)_3Cl(PPh_3)_2](BF_4)$. Although the reduction products were not identified in the above study,[62] by analogy with other data[58] one can assume that the $Me^+$ and $Et^+$ ions are reduced as a result of the reaction.

A brief survey of the applications of triphenylcarbenium salts in the chemistry of organometallic compounds has been published.[63] We shall quote only a few additional examples.

The reaction




has been carried out.[64] The carbene complex has been isolated analogously in the oxidation of the dithiane derivative:[65]




A μ-methylidyne compound is formed from a complex with a bridging methylene ligand:[66,67]

$$[Cp_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CH_2)] + Ph_3C^+PF_6^- \xrightarrow{CH_2Cl_2} \rightarrow [Cp_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CH)](PF_6) + Ph_3CH.$$

The initial complex can be regenerated by treating the final product with $Li[HBEt_3]$.

The question of the mechanism of hydride shifts has been the subject of a controversy. It has been noted in a monograph[68] that the hydride shift reaction can take place in either one or two steps:

$$B^+ + H{-}A \rightarrow BH + A^+;$$
$$B^+ + H{:}A \rightarrow B^{\cdot} + [HA]^{\cdot+} \rightarrow BH + A^+$$

In several studies the possibility of a hydride shift via a mechanism involving a one-electron transfer has been demonstrated. The question of the extent to which this mechanism occurs has so far remained open.[68]

The ability of the trityl cation to interact with an inner-sphere hydride ion can be clearly demonstrated in relation to the complex $[RuH_2(PPh_3)_4]$.[69] Treatment of the complex with a calculated amount of $Ph_3C^+PF_6^-$ yielded $[RuH(PPh_3)_4].(PF_6)$. Oxidation of the hydride ligand can lead to the

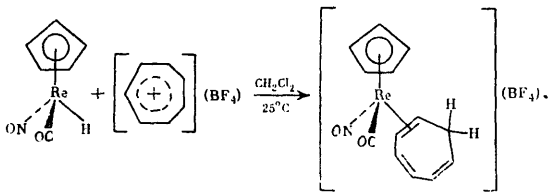
formation of the bridged complex[70]

$$2\,(Ph_4As)\,[HCr(CO)_5] + Ph_3C^+BF_4^- \xrightarrow{THF} \rightarrow (Ph_4As)\,[(CO)_5Cr(\mu\text{-}H)Cr(CO)_5] + Ph_3CH + [Ph_4As](BF_4).$$

It has been demonstrated convincingly[71] that the character of the product of the reaction between $Ph_3C^+X^-$ ($X = BF_4$ or $PF_6$) and the hydride compound $[CpW(NO)_2H]$ depends on the electron-donating capacity of the solvent. Thus the solvato-complex $[CpW(NO)_2(MeCN)]X$ is formed in acetonitrile, while the dimer $[Cp_2W_2(NO)_4H]$ is produced in dichloromethane, which has no electron-donating properties. The oxidation of the hydride ligand in the complexes $\{Mn(CO)_3[P(OMe)_3]_2H\}$ [72] and $[Cp(CO)_3MH]$ ($M = Mo$ or W) [73] by $Ph_3C^+PF_6^-$ in $CH_2Cl_2$ leads to the deposition of the compounds $\{Mn(CO)_3[P(OMe)_3]_2(FPF_5)\}$ and $[Cp(CO)_3M.(FPF_5)]$ respectively in the solid phase. These compounds are formed because the solvent cannot compete with the $PF_6^-$ anion for a site in the inner coordination sphere. The reaction of the rhenium complex $[CpRe(CO)(NO)H]$ with triphenylcarbenium tetrafluoroborate in $CH_2Cl_2$ affords $[CpRe(CO)(NO)(\eta_2\text{-}PhCHPh_2)](PF_6)$ as the final product.[74]

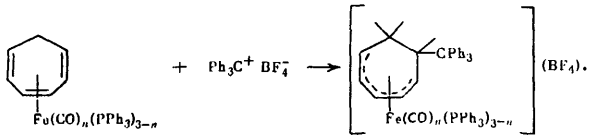
Apart from trityl cations, other carbenium ions can also be used as hydride ion acceptors in preparative coordination chemistry. Although the tropylium cation is a much less active hydride ion acceptor than the triphenylcarbenium cation,[68] nevertheless the oxidation of the cluster anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ by the tropylium ion has been described.[75] This reaction involves the abstraction of the hydride ligand and the formation of the compound $[Re_3(\mu\text{-}H)_3(CO)_{10}L_2]$ in the presence of carbon monoxide ($L = CO$) or an electron-donating solvent ($L = MeCN$). In the absence of electron donors, in the inert dichloromethane, the complex $[Re_3H_2(CO)_{10}(\eta_5\text{-}C_7H_9)]$ is formed in a satisfactory yield.

The interaction of tropylium tetrafluoroborate with the complex $[CpRe(CO)(NO)H]$ leads to the dehydrogenation of the complex and subsequent coordination of the triene formed:[76]



Dehydrogenation of the complex $[CpOs(CO)_2H]$ by tropylium tetrafluoroborate in $CH_2Cl_2$ at 25 °C for 6 days gives rise to $[CpOs(CO)_2(1,2\text{-}\eta_2\text{-}C_7H_8)](BF_4)$ in 80% yield.[77]

In conclusion of this Section, we may note that the trityl cation can alkylate coordinated ligands, for example:[78,79]



## V. PROTIC ACIDS

In studies in non-aqueous solvents the proton can function as a one-electron oxidant. Thus metallic titanium or chromium are oxidised by $HBF_4$ in acetonitrile with formation of $[Ti(MeCN)_6](BF_4)_3$ and $[Cr(MeCN)_x](BF_4)_3$.[80] When zerovalent molybdenum hexacarbonyl $Mo(CO)_6$ was refluxed with anhydrous formic acid for 3 h in diglyme, $Mo_2(O_2CH)_4$ was isolated in 65% yield.[81] The complex $[CpRh(PPh_3).(PhC_2Ph)]$ reacts with an excess of trifluoroacetic acid at 40 °C with displacement of the acetylenic ligand and the formation of the oxidation product $[CpRh(PPh_3)(O_2CCF_3)]$.[82]

The reaction of the dimeric complex $[CpCr(NO_2)]_2$ with two moles of $HBF_4OMe_2$ in dichloromethane leads to oxidative cleavage with formation of the monomeric compound $CpCr(NO)_2BF_4$, which is converted into the stable complex $[CpCr(NO)_2(MeCN)](BF_4)$ on treatment with acetonitrile.[9] Similarly the interaction of the isoelectronic complex $[CpFe(CO)_2]_2$ with toluene-*p*-sulphonic acid in acetonitrile leads to oxidative cleavage of the Fe–Fe bond and formation of the solvato-complex $[CpFe(CO)_2(MeCN)](O_3SC_6H_4Me)$.[84] It was assumed in the above study that the protic acid is in fact responsible for the oxidation of the complex. However, the evolution of free hydrogen was not observed.

Together with triphenylcarbenium and silver salts, protic acids are used to oxidise the $H^-$ ion in hydride complexes. It has been established[85] that $MoH_4(PMePh_2)_4$ reacts with $HBF_4$ or $HBF_6$ in THF to form the cation $[MoH_3(PMePh_2)_3]^+$. The reactions with the weaker acids $CF_3CO_2H$ or $p\text{-}MeC_6H_4SO_3H$ in toluene lead to the formation of the compounds $[MoH_2(CF_3CO_3)_2(PMePh_2)_3]$ and $[MoH_2.(p\text{-}MeC_6H_4SO_3)_2(PMePh_2)_3]$. The complex $[CpW(NO)_2H]$ is oxidised by anhydrous toluene-*p*-sulphonic acid in THF to $[CpW(NO)_2(OSO_2C_6H_4Me)]$.[86] The interaction of the complex $[H_2RhCp(PPr_3)]$ with trifluoroacetic acid in methanol in the presence of $NH_4PF_6$ entails a rapid reaction accompanied by the evolution of hydrogen and the formation of the dinuclear complex $[Cp(PPr_3)Rh(\mu\text{-}H)_3Rh(PPr_3)Cp](PF_6)$.[82] The interaction of tungsten, rhenium, osmium, and iridium polyhydride compounds with $HBF_4.OEt_2$ in acetonitrile has been investigated.[87] The initial compounds and the final products of the syntheses are presented schematically below:[87]

$$WH_6(PMe_2Ph)_3 \rightarrow [WH_2(MeCN)_3(PMe_2Ph)_3]^{2+};$$
$$ReH_5(PMe_2Ph)_3 \rightarrow [ReH(MeCN)_3(PMe_2Ph)_4]^{2+};$$
$$ReH_7(PPh_3)_2 \rightarrow [ReH(MeCN)_4(PPh_3)]^{2+};$$
$$OsH_4(PMe_2Ph)_4 \rightarrow [Os(MeCN)_3(PMe_2Ph)_3]^{2+};$$
$$IrH_5(PPh_3)_2 \rightarrow [IrH_2(MeCN)_2(PPh_3)_2]^+.$$

The authors concluded[87] that the central atoms in the complexes $WH_6(PMe_2Ph)_3$ and $ReH_7(PPh_3)_2$ have the $d^0$ electronic configuration. The protonation of the metal ion in such compounds is therefore hardly to be expected. It is most likely that the interaction with $H^+$ leads to the formation of the $M...H...H^+$ linear intermediate. On the other hand, the complexes $OsH_4(PMe_2Ph)_3$, $ReH_5(PMe_2Ph)_3$, and $IrH_5.(PPh_3)_2$ are more likely to be protonated at the metal atom. In all cases the protonated adducts are relatively unstable and decompose at room temperature with evolution of hydrogen and the vacant sites generated in the inner sphere are filled by solvent molecules. In the analysis of their own experimental and literature data on the acidolysis of the polyhydride compounds the authors[87] note that the biscationic complex is frequently stabilised as a result of the reaction. However, the causes of this phenomenon remain unelucidated.

The interaction of $[Mn(CO)_5]^-$ with trifluoromethanesulphonic acid in THF yielded the compound $HMn(CO)_5$,[88] which is a fairly strong acid ($pK_a = 7$).[89] Consequently, the hydrogen in $HMn(CO)_5$ has almost no hydride character. Nevertheless, the interaction of the complex $[(Ph_3P)_2N].[Mn(CO)_5]$ in the absence of a solvent with pure $CF_3SO_3H$ leads to the formation of the complex $Mn(CO)_5(SO_3CF_3)$ and

the evolution of hydrogen.[89] This reaction proceeds via the stage

$$HMn(CO)_5 + CF_3SO_3H \rightarrow Mn(CO)_5(SO_3CF_3) + H_2.$$

Thus, when the character of the medium is altered, a ligand, which does not exhibit the properties of a hydride in other solutions, is oxidised.

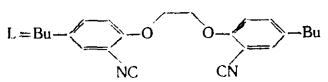
## VI. SILVER AND MERCURY SALTS

The importance of silver salts as dehalogenating agents has been emphasised in a review.[90] However, the salts AgX are also used as one-electron oxidants in syntheses in non-aqueous media. According to Rabinovich and Khavin,[91] the redox potential of the $Ag^+/Ag$ pair in aqueous solution is 0.799 V. There are no literature data on the redox potentials of the $Ag^+/Ag$ pair in weakly electron-donating solvents. This can probably be accounted for by the limited solubility of silver salts in such media.[92] In order to estimate the oxidising capacity of $AgBF_4$ in non-aqueous solvents, its reactions with $N(C_6H_4Br\text{-}p)_3$ ($E$ = 1.16 V), $NPh_3$ ($E$ = 0.88 V), and $Cp_2Fe$ ($E$ = 0.38 V) were investigated[92] in $CH_2Cl_2$, PhMe, MeCN, and THF. In all the solvents, ferrocene is oxidised to $[Cp_2Fe](BF_4)$, whereas amines are oxidised only by a suspension of $AgBF_4$ in dichloromethane. Consequently $AgBF_4$ is a powerful oxidant in $CH_2Cl_2$, but is milder in PhMe, MeCN, and THF, in agreement with their solvating capacities.

An important additional factor responsible for the application of silver salts in synthesis as oxidants is the possibility of the ready separation of the metallic silver formed on reduction from the reaction mixture. As a rule, reactions with participation of $Ag^+$ as the oxidant are rapid, are satisfactorily selective, and do not require an appreciable excess of this reagent.

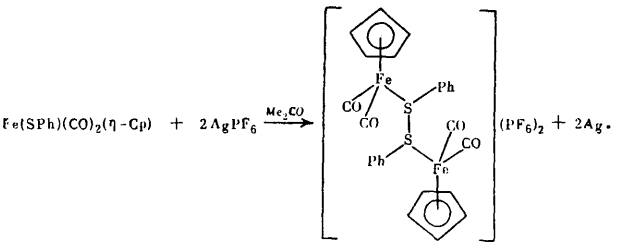
A manual recommends[53] that silver tetrafluoroborate be obtained from AgF and $BF_3$ by the method of Olah and Quinn.[93] The same compound can also be obtained by dissolving silver oxide in 45% $HBF_4$.[94] Silver perchlorate is obtained by the reaction of $Ag_2CO_3$ with 10% $HClO_4$. The synthesis involves filtration, the removal of water *in vacuo*, and azeotropic drying with benzene.[53]

The $Ag^+$ ion has been used in preparative coordination chemistry for a long time. For example, as early as 1923 Morgan[95] suggested that the complex $[Cu(MeCN)_6](NO_3)$ be prepared by oxidising metallic copper with $AgNO_3$ in acetonitrile. The extensive use of silver salts as oxidants began in the last decade. According to Treichel and Essenmacher,[96] the isonitrile complex of chromium $[Cr(CNPh)_6]$ is instantly oxidised in acetone by one equivalent of $AgPF_6$ with formation of $[Cr(CNPh)_6](PF_6)$. When the latter was allowed to interact with yet another equivalent of $AgPF_6$ or on interaction of the initial complex with two moles of silver hexafluoroborate, $[Cr(CNPh)_6](PF_6)_2$ was obtained. The chelate compounds $[CrL_3](PF_6)$ and $[CrL_3](PF_6)_2$ have been synthesised analogously:[97]




The oxidation of the complex $CpCo(PPh_3)_2$ by silver halides AgX (X = Cl, Br, or I) in THF led to the formation of the compounds $[CpCo(PPh_3)X]$.[98]

The oxidative dimerisation reaction, which proceeds via the oxidation of the ligand, has been investigated:[99]




The authors[99] suggest that the HOMO in the initial complex is localised mainly on the sulphur atom and not on the iron atom. The loss of one electron from this orbital leads to the formation of a radical species with the unpaired electron localised on the ligand. The final dimeric complex is formed from two such species. The central atom in the complexes $Fe(SPh)(CO)L(\eta\text{-}C_5R_5)$ is oxidised:

$$Fe(SPh)(CO)L(\eta\text{-}C_5R_5) + AgX \rightarrow [Fe(SPh)(CO)L(\eta\text{-}C_5R_5)]X + Ag;$$
$$R=Me,\ L=CO,\ PMe_3,\ PMe_2Ph,\ PMePh_2;$$
$$R=H,\ L=PMe_3,\ PMe_2Ph,\ PMePh_2.$$

Numerous examples of the oxidation of organometallic compounds with silver salts have been described in a book.[100]

The possibility of the oxidation of the hydride complexes $[MoH_4L_4]$ (L = $PMe_2Ph$ or $PMePh_2$) by silver tetrafluoroborate in acetonitrile has been demonstrated:[101]

$$[MoH_4L_4] + 2AgBF_4 + 2MeCN \rightarrow [MoH_2L_4(MeCN)_2](BF_4)_2 + H_2 + 2Ag.$$

The reactions reached completion in several minutes and the products were obtained in satisfactory yields.

Mercury salts together with silver salts can be used in experiments in non-aqueous solvents as oxidants. Like the $Ag^+$ ion, the $Hg^{2+}$ ion has a relatively high oxidising capacity. In both cases the reduction products, namely metallic silver and mercury, can be readily separated from the reaction mixture. The oxidation of the lanthanides Sm, Er, Yb,[102] Sc, and Y [103] by $HgCl_2$ in THF yielded the tetrahydrofuranates of the corresponding trichlorides:

$$2Ln + 3HgCl_2 + 6THF \rightarrow 2LnCl_3 \cdot 3THF + 3Hg.$$

The complex $[Cr(CO)_5(O_2CCF_3)]^-$ is formed as a result of oxidative substitution by mercury trifluoroacetate:[104]

$$[Cr_2(CO)_{10}]^{2-} + Hg(O_2CCF_3)_2 \rightarrow 2[Cr(CO)_5(O_2CCF_3)]^- + Hg.$$

## VII. AMINE OXIDES

The ability of the $CO_2$ molecule to be coordinated to metal ions is known to be appreciably weaker than that of carbon monoxide. For this reason, one of the methods of the specific elimination of CO from metal carbonyl compounds involves the oxidation of a carbonyl ligand to $CO_2$ with subsequent substitution of this molecule by some stronger electron donor (in particular, a solvent molecule). Trimethylamine oxide is nowadays used widely for the oxidation of the coordinated CO molecule.

The above reagent is formed in 95% yield as the dihydrate $Me_3NO.2H_2O$ on oxidation of $Me_3N$ by hydrogen peroxide:[105,106]

$$Me_3N + H_2O_2 + H_2O \rightarrow Me_3NO \cdot 2H_2O.$$

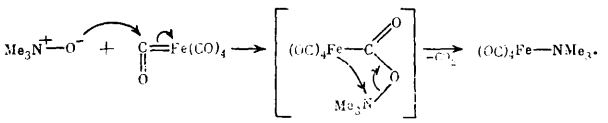
Total dehydration gives rise to the extremely hygroscopic product $Me_3NO$.[106,107] The ability of amine oxides to react with metal carbonyls was first demonstrated by Heiber and Lipp[108] and Alper and Edward.[109] In particular, it has been

established[109] that aliphatic, aromatic, or heterocyclic amine oxides are reduced to the corresponding amines on interaction with $Fe(CO)_5$. The amines have been isolated from the reaction mixture and characterised. Iron oxides have also been obtained in the synthetic reactions. It was suggested in 1974 [110] that the reactions of amine oxides with metal carbonyls be used for the decomposition of the complex and the isolation of the organic ligand. Thus, when the complexes $[LFe(CO)_3]$ [L = $C_8H_8$, norbornadiene,[110] or $C_7H_6NN(H)C_6H_4NO_2$ [111]] in benzene or acetone react with an excess of $Me_3NO$ or $Me_3NO.2H_2O$, complete decarbonylation with decomposition of the complexes takes place. The free ligands L have been isolated in 75–95% yields. The reaction of $Me_3NO$ with $Fe(CO)_5$ in the presence of bidentate diene ligands L yielded substituted complexes $[LFe(CO)_3]$:[112]

$$Fe(CO)_5 + Me_3NO + L \rightarrow [LFe(CO)_3] + Me_3N + CO_2 + CO.$$

Since then the reactions involving decarbonylation by amine oxides have been used for preparative purposes.

In the interaction of $Fe(CO)_5$ with a twofold excess of $Me_3NO$ in THF at −30 °C, evolution of $CO_2$ was observed; the complex $Fe(CO)_4(NMe_3)$ was obtained from the reaction mixture in 45% yield;[113] a mechanism for the oxidative decarbonylation, involving nucleophilic attack by $Me_3NO$ on the carbon atom of the carbonyl ligand, has been proposed on the basis of the results:[107,113]

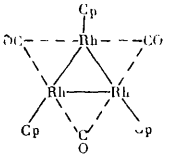


Many instances of oxidative decarbonylation reactions using amine oxides, some of which have been published in a review,[106] are known at present in the literature. It has been noted[107] that these reactions can be carried out in a wide range of solvents such as benzene, dichloromethane, chloroform, THF, acetonitrile, acetone, 2-methoxyethanol, and methanol.

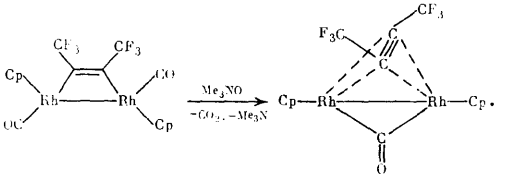
We shall present certain examples of the reactions involving the selective oxidation of CO in metal carbonyls. The interaction of $[W(CO)_5(PPh_3)]$ with $Me_3NO$ in dichloromethane in the presence of $SMe_2$ led to the formation of $[W(CO)_4(PPh_3).(SMe_2)]$.[114] The reaction of $[Ru(CO)_2Cl_2bipy]$ (bipy = 2,2′-bipyridyl) with $Me_3NO$ in molar proportions of 1:5 in pyridine formed the monosubstitution product $[Ru(CO)PyCl_2.bipy]$.[115] The authors of the above study point out that the attempts at the complete decarbonylation of $[Ru(CO)_2.Cl_2bipy]$ were unsuccessful. Refluxing of the homodinuclear complex $[Mn_2H(CN)(CO)_5Dppm]$ with an excess of $Me_3NO.2H_2O$ in a dichloromethane–methanol mixture for 88 h leads to the formation of the complex $[Mn_2H(CN)(CO)_4Dppm]$ in 24% yield; irradiation of the reaction mixture with visible light increases the rate of reaction and the yield of the final product.[116] Data on the oxidative decarbonylation of cluster compounds may be found in a number of publications.[107,117–124]

If the oxidative decarbonylation is carried out in the presence of electron-donating solvents, the reaction can influence the formation of solvato-complexes. For example, the removal of a carbonyl group from the triosmium cluster $Os_3(CO)_{12}$ with the aid of trimethylamine oxide in the presence of acetonitrile leads to the formation of the monosolvate $Os_3(CO)_{11}(MeCN)$. The reaction of $Os_3(CO)_{11}(MeCN)$ with yet another mole of $Me_3NO$ gives rise to a high yield of $Os_3(CO)_{10}(MeCN)_2$.[119,120] The reaction does not proceed further and the trisolvate is not formed. According to the authors, this can be explained by the mutual influence of the ligands, which reduces the tendency of the carbonyl centres to undergo nucleophilic attack.

In the absence of an electron-donating ligand (or an electron-donating solvent) the coordination-unsaturated species formed as a result of the removal of CO can react with the initial compound to form a metal–metal bond.[125] Thus the interaction of $Me_3NO$ with $CpRH(CO)_2$ in benzene leads to the formation of the trimer as the dominant product:

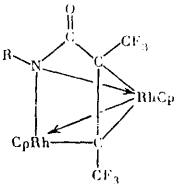


The decarbonylation of the complex $(\eta\text{-}Cp)_2Rh_2(CO)_2.(CF_3C_2CF_3)$ by trimethylamine oxide in dry acetone is accompanied by the rotation of the coordinated alkyne by 90° and the remaining coordinated carbonyl occupies a bridging position:[126–128]



The interaction of $Ru_2(CO)_6(DAB)$ (DAB = 1,4-substituted 1,4-diazabuta-1,3-diene) with trimethylamine oxide in a mixture of non-electron-donating solvents (dichloromethane and toluene) leads to the formation of the compound $Ru_2.(CO)_5(DAB)$.[129] The reaction alters the type of binding of the DAB ligand: instead of the 6e-($\sigma$-N, $\mu^2$-N′, $\eta^2$-C=N′) coordination, we have the coordination 8e($\sigma$-N, $\sigma$-N′, $\eta^2$-C=N, $\eta^2$-C′=N′).

Many chemical properties of inner-sphere organic isocyanides are known to resemble those of coordinated carbon monoxide.[130] In a recently published study,[131] trimethylamine oxide was used to oxidise the isocyanide ligand RNC (R = Me, Bu, Pr, $C_6H_{11}$) coordinated to a rhodium atom in the complex $[(\eta^5\text{-}Cp)_2Rh_2(CO)(CNR)(CF_3C_2CF_3)]$. The oxygen is then transferred from $Me_3NO$ to the isocyanide with formation of the isocyanate RNCO. The subsequent intramolecular rearrangement and evolution of CO results in the formation of a compound which has the following structure according to X-ray diffraction data:



## VIII. OTHER OXIDANTS

Among other oxidants, mention should be made of the higher halides of Group V elements. Thus the oxidative halogenation of the complex $[Mo(\mu\text{-}C_8Me_8)Cp_2]$ by the mild oxidants $[NPr_4](SbCb_6)$ or $[PhCO](SbCl_6)$ in dichloromethane leads to the formation of the complex $[Mo(\mu\text{-}C_8Me_8).(\mu\text{-}Cl)Cp_2](SbCl_4)$ in a quantitative yield.[132] The authors[132]

suggest that the final product is obtained as a result of oxidation which is followed by the halogenation of the cation formed.

In order to obtain complexes with a coordinated $SO_2$ molecule, $AsF_5$ is widely used.[133-135] Thus the reaction of metallic zinc or cadmium with an excess of arsenic pentafluoride in liquid $SO_2$ leads to the formation of homogeneous solvato-complexes:[134,135]

$$M + 3AsF_5 \xrightarrow{SO_2} [M(SO_2)_2](AsF_6)_2 + AsF_3.$$

The complexes $[M(SO_2)_2(AsF_6)_2]_n$ have been obtained by the interaction of the metal M (M = Mn, Fe, Co, Ni, Cu, Zn, or Mg) and $AsF_5$ in molar proportions of 1:5 in liquid $SO_2$.[133]

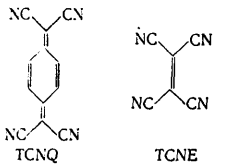
Organic 1,2-dihalides can oxidise certain metals. For example, the slow addition of Sm or Yb to a solution of 1,2-diiodoethane in THF leads to the formation of $SmI_2$ and $YbI_2$ in quantitative yields:[136]

$$M + ICH_2CH_2I \xrightarrow{THF} MI_2 + CH_2CH_2.$$

The reaction is rapid at room temperature.

A mixture of $AlCl_3$ and $CH_2Cl_2$ exhibits fairly strong oxidising properties.[137-139] Unfortunately the authors did not consider the oxidation mechanism and did not identify the reduction products. $AlCl_3$ in dichloromethane has been used to oxidise the molybdenum complex $[Mo(CO)_2(bipy)_2]$. After the completion of the reaction, the product was precipitated in the form of the dimer $[Mo(CO)_2(bipy)_2]_2 \cdot (BF_4)_2$ by adding $NaBF_4$ to the reaction mixture.[140]

Tetracyanoquinodimethane (TCNQ) and tetracyanoethylene (TCNE)

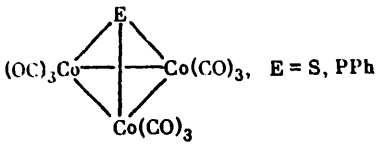


TCNQ

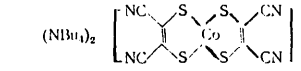


TCNE

are known to be fairly strong electron acceptors.[141,142] Stable radical-anions $TCNQ^-$ and $TCNE^-$ are formed in one-electron reduction. The half-wave potentials of the polarographic reduction of these compounds in acetonitrile (0.127 V for TCNQ and 0.152 V for TCNE) show that they are mild oxidants in the given solvents.[142] It has been established in a recently published study[143] that the clusters



react with TCNQ in ethanol, acetone, dichloroethane, THF, or dichloromethane to form the one-electron oxidation product $[ECo_3(CO)_9]^+$. TCNE oxidises the complex



with formation of the dimeric compound $[NBu_4)_2 \cdot [Co(C_4N_2S_2)_2]_2$.[144]

Organic disulphides can oxidise metal carbonyls in a photochemical reaction in accordance with the equation

$$[CpM(CO)_n]_2 + S_2R_2 \xrightarrow{h\nu} 2[CpM(CO)_n SR];$$

M = Fe, R = Me, $n$ = 2 (Ref.145);

M = Ru, R = Me, Ph, Bz, $n$ = 2 (Ref.146);

M = W, R = $Me_2NC(S)$, $n$ = 3 (Ref.147).

The mechanism of processes of this kind involves the formation of extremely reactive metal carbonyl radicals as a result of photolysis, which are oxidised in a dark reaction by the organic disulphide with formation of thiolate complexes.[147]

In conclusion, one should note that many oxidants can be used in both aqueous and non-aqueous solutions. Thus instances of the employment of $PbO_2$ in a mixture of MeCN and $CF_3CO_2H$,[148] of $Cp_2Fe^+$ in acetonitrile[149,150] and THF,[151-153] of $Pb(OAc)_4$ in dichloromethane,[154] of $TiCl_3$ in dichloromethane,[155,156] etc. are known. The procedure involving the modification of "traditional" oxidants in order to impart hydrophobic properties to the latter is of interest. For example, the pyridine analogue of potassium dichromate, namely $(PyH)_2Cr_2O_7$, has been synthesised.[157] This compound is highly soluble in dimethylformamide, diethylacetamide, and dimethyl sulphoxide and is sparingly soluble in dichloromethane and chloroform. An analogue of hydrogen peroxide, namely the compound $(Me_4N)_2O_2$, is used to synthesise complexes in acetonitrile.[158]

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# Thermochemistry of Organic and Organohalogen Compounds†

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The advances in the thermochemistry of organic compounds, mainly cyclic and organohalogen derivatives, are examined. Studies on the thermodynamics of the polymerisation reactions of cyclic compounds, the determination of the standard enthalpies of formation of cyclic and organohalogen compounds, and the determination of relations between the standard enthalpies of formation and the strain energies of molecules, on the one hand, and their structure, on the other are analysed in detail.
The bibliography includes 213 references.

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## I. INTRODUCTION

Fundamental research into the thermochemical properties of organic compounds is traditional in Russian thermochemistry. The determination of the heats of combustion of organic compounds in a bomb calorimeter was the fundamental experimental method at the Laboratory of Thermochemistry founded at Moscow State University (1891) by V.F.Luginin.[1,2]

After Luginin, his student and collaborator P.V.Zubov continued the research into the thermochemistry of organic compounds.[3-7] M.M.Popov made a major contribution to the development of the methods for the determination of heats of combustion. Together with W.Świętosławski, he proposed in 1914 that a single primary standard, benzoic acid, be used for the calibration of calorimeters.[8] In 1934 Popov and Shirokikh[9] constructed the first calorimeter with a moving bomb and thereby introduced into calorimetric practice a new method, which proved to be exceptionally useful for the investigation of organohalogen, organosulphur, organosilicon, and organometallic compounds as well as many other substances with a relatively complex composition.

The studies of S.M.Skuratov and his co-workers, in the course of which a self-sealing bomb calorimeter was constructed and a new model of a highly sensitive mercury thermometer was used, led to the creation of precision calorimetric apparatus which differed little from modern apparatus.[10,11] The sharp increase in the accuracy of the determination of the heats of combustion made it possible to observe extremely fine energetic effects (the mutual influence of atoms and groups, the differences between the properties of isomers, etc.). Further improvement of the apparatus and methods for stationary bomb calorimeters involved the improvement of the means for the measurement of temperature, the technique of the calorimetric experiment, and the analytical part of the thermochemical experiment.[12-14]

†In 1984, 150 years elapsed since the date of the birth of the famous Russian chemist, V.F.Luginin, who was a student of M.Berthelot and professor of Moscow University. The review has been written to commemorate this jubilee.

The standard enthalpies of formation of gaseous lower fluoro- and chlorofluorohydrocarbons have been determined mainly by two methods: by measuring the enthalpy of reaction with alkali metals ($\Delta H$) [15,16] and by measuring the standard enthalpy of combustion in oxygen ($\Delta H_c^\circ$).[17,18]

Table 1. The specific combustion energies of standard substances at 298 K.

| Substance* | $-\Delta U_c^0/M$, J g$^{-1}$ | | | |
|---|---|---|---|---|
| | data from Laboratory of Thermochemistry at Moscow State University | refs. | data of other workers | refs. |
| Succinic acid (s) | 12638.3±3.4 | [10] | 12638.5±1.5** | [28] |
| *p*-Chlorobenzoic acid (s) | 19569.4±3.8 | [19] | 19566.6±1.9** | [28] |
| α-D-Glucose (s) | 15559.7±3.0 | [26] | 15557.9±1.6 | [29] |
| ααα-Trifluorotoluene (l) | 23058.6±2.9 | [27] | 23064±14 | [30] |
| | | | 23051.2±2.8 | [31] |

*Here and henceforth the state of the substance is indicated in brackets: (l) = liquid, (s) = solid, and (g) = gaseous.
**Values recommended by the Mendeleev All-Union Institute of Metrology.

As the range of substances investigated was extended and the experimental technique improved, the importance of the method of combustion in oxygen increased continuously in view of its universality. The improvement of the method of determining the energies of combustion in rotating bomb calorimeters made it possible to apply it in the study of a whole series of new groups of organohalogen compounds: for substances containing different groups of halogens (for example, $CF_3CHClBr$ and $CF_2BrCHFCl$), for gaseous and volatile Freons (for example, $CF_2ClCFCl_2$, $CF_2ClCCl_3$, and $CF_2ClCF_2Cl$), for perfluoro-compounds, etc.[19-21] The development of methods for the combustion of gaseous substances in the liquefied state in a bomb calorimeter, first used in experiments designed to determine the combustion energy of chlorotrifluoroethylene,[22] occupies a special place.

The validity of the results obtained has been confirmed by the analysis of the literature data.[20,23-25] The method for the determination of the enthalpies of combustion of liquefied gases has led to extensive possibilities for the investigation of the thermochemical properties of substances which are not fully combusted in the gaseous state in the bomb.

The reliability of the methods for the determination of the energies of combustion of organic and organohalogen substances in stationary and rotating bomb calorimeters has been demonstrated by measuring the energies of combustion of secondary standards and highly pure specimens of thoroughly investigated substances (Table 1).

In the present review we were naturally unable to analyse all the available experimental data on the thermochemistry of organic and organohalogen compounds and we were obliged to confine ourselves to the aspects of the field which have been developed at the Laboratory of Thermochemistry at Moscow State University with inclusion of literature data for related thermochemical fields. Almost the entire data in the review can be arranged in terms of three principal branches of thermochemistry: the thermochemistry of the polymerisation reactions of heterocyclic compounds, the thermochemistry of cyclic hydrocarbons and their derivatives, and the thermochemistry of organohalogen compounds. The development of each has been stimulated by the urgent requirements of industry.

## II. UNITS OF MEASUREMENT, AUXILIARY QUANTITIES, AND CALCULATION OF THE STRAIN ENERGY

The enthalpies of formation of organic and organohalogen compounds ($\Delta H_f^\circ$) quoted in this review constitute a system of mutually consistent quantities. In order to ensure this, all the enthalpies of formation have been recalculated on the basis of key quantities selected by the International Commission from the most reliable studies carried out in recent years and recommended by CODATA.[32] Since the values recommended by CODATA for certain key quantities (for example the $\Delta H_f^\circ$ for HF solutions) differ significantly from those adopted earlier,[33,34] the values of $\Delta H_f^\circ$ for organofluorine compounds presented in this review also frequently differ from those published in experimental or review communications.

All the thermochemical quantities in the present review are expressed in Joules in conformity with the international SI system of units. The data quoted in the original communications in calories have been recalculated on the basis of the relation 1 cal = 4.184 J.[35] The atomic weights have been adopted on the basis of IUPAC tables.[36] The enthalpies of dilution of HF and HCl solutions have been taken from Johnson et al.[37] and Cox et al.[38] respectively. The heat capacities of the individual substances have been taken from a handbook[33] and the heat capacities of solutions from Parker.[39]

The strain energies $E_S$ of cyclic compounds, considered in this review, were obtained as differences between the experimental $\Delta H_f^\circ$ and quantities calculated assuming additivity for unstrained acyclic molecules with the same number and character of bonds:

$$E_s = \Delta H^\circ_{f,(g),e} - \Delta H^\circ_{f,(g),c},$$

where $\Delta H_f^\circ$, (g), e is the experimental standard enthalpy of formation of the gaseous compound and $\Delta H_f^\circ$, (g), c the calculated value equal to the sum of the corresponding group contributions taken from Benson et al.[40] For certain groups of compounds, the $E_S$ were calculated analogously as the differences between the experimental and calculated enthalpies of combustion. The contribution of the $-CH_2-$ groups to $\Delta H^\circ_{c(g)}$ in these calculations was assumed to be $-658.63$ kJ mol$^{-1}$;[40] the contributions due to other groups are listed in the corresponding Tables in this review. In certain specially stipulated cases it proved possible to calculate the $E_S$ only for the liquid state; in this case the contributions of the $-CH_2-$ group were taken from Prosen and Rossini[41] and Skuratov.[42]

Such calculation yields conventional values of $E_S$, because the result depends on the choice of the additive scheme for the calculation of the $\Delta H_f^\circ$ for the unstrained analogue and in addition the calculation does not take into account the difference between the thermal and zero-point energies and also the difference between the internal energies and the enthalpies for the real cyclic molecule and the hypothetical molecule adopted as the unstrained species. The influence of these energy differences, which have not been allowed for, on $E_S$ has been examined;[43] it is relatively small and is approximately constant in each series of cyclic compounds, so that, when the values of $E_S$ are compared for compounds of a single series, the error arising due to the failure to take them into account is insignificant.

Questions associated with the nature of the strain and the complications arising in the quantitative analysis of the $E_S$ have also been examined in a number of studies.[44-46]. The conventional nature of the $E_S$ does not preclude the comparison and discussion of the reactivities of compounds of a single series[47] and of the dependence of the $\Delta H_f^\circ$ on their structure.[43,48]

The values of $\Delta H_c^\circ$, $\Delta H_f^\circ$, and $E_S$ presented below refer to 298.15 K (except for specified cases). The errors in the thermochemical quantities are expressed in terms of a 95% confidence interval.

## III. THERMOCHEMISTRY OF THE POLYMERISATION REACTIONS OF HETEROCYCLIC COMPOUNDS

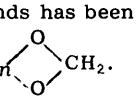
The study of the thermodynamic properties of lactams and their *N*-methyl-substituted derivatives is of great interest from the standpoint of the investigation of the capacity of these compounds for polymerisation. The reactivity of heterocyclic compounds is known to depend greatly on the number of members in the ring. This has also been observed for a series of lactams whose capacity for polymerisation diminishes consistently on passing from an eight-membered ring (ζ-enantholactam) to a five-membered ring (α-pyrrolidinone).[49] The ability of lactams to polymerise can be rigorously characterised by the Gibbs free energy of polymerisation at the corresponding temperature. In order to determine this quantity, direct measurement of the enthalpy of polymerisation and the measurement of the absolute entropies of the monomers and polymers are normally required; both sets of measurements are extremely laborious and are not always possible.

However, it is possible to make a significant approach to the solution of this problem by employing the enthalpies of combustion of the monomers. Thus it has been shown[49] that one of the factors determining the different capacities of lactams for polymerisation is the ring strain energy $E_S$. The values of $E_S$ calculated[49] from the experimental enthalpies of combustion of lactams using data[50] for ζ-enantholactam, ε-caprolactam, α-piperidinone, and α-pyrrolidinone at 75 °C are 22.2, 15.9, 9.2, and 4.6 kJ mol$^{-1}$ respectively. The decrease of $E_S$ with decrease in the number of members in the ring ($8 > 7 > 6 > 5$) varies in parallel with the capacity of lactams for polymerisation.

Direct measurement of the enthalpies of polymerisation of caprolactam and enantholactam[42,51] and also the calculation of the enthalpies of polymerisation of these substances from the experimental $\Delta H_c^\circ$ of the polymer and monomer[52] led to values which agreed, within the limits of error, with the $E_S$ taken from Strepikheev et al.[49]. Strepikheev et al.[49] also demonstrated, in relation to 5- and 7-methylcaprolactams, that the substitution of a hydrogen atom in the methylene group by the methyl group does not affect significantly the ring strain.

Substitution at the N atom reduces the capacity of lactams for polymerisation to a greater extent than substitution at a C atom.[53] It has been suggested that N-substituted lactams are in general unable to polymerise, but it was later established that *N*-methylenantholactam nevertheless undergoes the polymerisation reaction.[54] The strain energies of *N*-methyl-lactams have been calculated[55] from the experimental enthalpies of combustion $\Delta H_c^\circ$(liq.); at 298 K they are 16.1, 9.2, −2.6, and −2.7 kJ mol$^{-1}$ for compounds containing between 8 and 5 members in the ring respectively. These data show that *N*-methyl lactams have significantly lower $E_S$ than their unsubstituted analogues. The highest $E_S$ has been observed for *N*-methylenantholactam; it is approximately equal to $E_S$ for the unsubstituted ε-caprolactam. In both series of compounds, at temperatures in the range 200–250 °C and a pressure of 100 kPa, the substances do not polymerise in the presence of activators if $E_S$ < 12 kJ mol$^{-1}$.[55]

For a more accurate description of the ability of substances to polymerise, it is necessary to take into account the entropy of this reaction. Since the entropies for unsubstituted lactams and certain polymers have been measured experimentally,[52] there is a possibility of testing and revising earlier conclusions. Comparison of the thermodynamic functions calculated[52] for the polymerisation reactions of four lactams shows that there is no significant difference between the $\Delta H$ and $\Delta G$ for the polymerisation of caprolactam and enantholactam and that in these cases allowance for the entropy term does not influence the conclusions reached above on the basis of the analysis of the $E_S$ alone. For the polymerisation reactions of α-pyrrolidinone and α-piperidinone, the difference between the enthalpies and Gibbs free energies is appreciably greater, because in this case the entropy of reaction $\Delta S$ is large. However, here too the qualitative conclusions reached from the analysis of the $E_S$ remain in force. Furthermore, since the entropies of α-pyrrolidinone and α-piperidinone are greater than the entropies of the corresponding linear polymers, allowance for the entropy term for the polymerisation reactions of these substances makes the Gibbs free energies of both reactions positive.

The thermochemistry of the polymerisation reactions of oxygen-containing compounds has been studied in relation to the cyclic formals  . The enthalpies of combustion and the strain energies for these substances are presented in Table 2. In the calculation of $E_S$, the contribution of the -O–$CH_2$–O- group to the standard enthalpy of combustion in the gaseous state $\Delta H_c^\circ$(gas) = −395.1 kJ mol$^{-1}$ was calculated as the difference between the values of $\Delta H_c^\circ$(gas) for di-n-butyl formal (Table 2) and n-octane (−5512.05 ± 2.9 kJ mol$^{-1}$ [50]). The enthalpies of evaporation required for the calculation of $\Delta H_c^\circ$(gas) have been calculated[57] from the semiempirical formulae quoted by Heukelom.[60] The standard enthalpies of evaporation $\Delta H_v$ were adjusted to 298 K on the basis of Watson's formula.[61] For comparison, the $E_S$ for cyclanes are also quoted in Table 2; the similarity of the dependences of $E_S$ on *n* for these two series is evident.

It follows from Table 2 that the strain energies of the formals investigated depend greatly on the number of members in the ring and decrease in the sequence 8 > 5 > 7 > 6. The equilibrium polymerisation of cyclic formals at 100–150 °C has been investigated[62] and it follows from the results that the capacity of cyclic formals for polymerisation decreases in the sequence 8 > 7 > 5 > 6 as a function of the number of members in the ring, i.e., as in the case of lactams, is largely determined by the strain energy.

Table 2. The enthalpies of combustion and evaporation and the strain energies of cyclic formals at 298 K (in kJ mol$^{-1}$)**.

| Substance | *n** | $-\Delta H_c^0$(l) | $\Delta H_v^?$ | $-\Delta H_c^0$(g) | $E_S$ | |
|---|---|---|---|---|---|---|
| | | | | | formals | cyclanes |
| Ethylene formal (l) | 5 | 1700.4±4.2 [56] | 35.6±0.4 [56] | — | — | — |
| | 5 | 1704.8±0.5 [57] | 33.5 [57] | 1738.3 | 25.7 | 26.4 |
| Trimethylene formal (l) | 6 | 2322.1±5.8 [56] | 35.6±0.8 [56] | — | — | — |
| | 6 | 2340.8±0.6 [58] | — | — | — | — |
| | 6 | 2331.9±0.8 [59] | — | — | — | — |
| | 6 | 2331.4±0.8 [57] | 38.5 [57] | 2369.9 | −1.1 | 0 |
| Tetramethylene formal (l) | 7 | 3008.8±0.9 [57] | 40.2 [57] | 3049.0 | 19.4 | 26.8 |
| Pentamethylene formal (l) | 8 | 3697.7±1.1 [57] | 43.9 [57] | 3741.6 | 53.3 | 41.4 |
| Di-n-butyl formal (l) | — | 5850.2±1.8 [57] | 56.9 [57] | 5907.1 | — | — |

Note. In this and subsequent tables the references are given to the original studies in which the experimental $\Delta H_c^\circ$ or $\Delta H_v^\circ$ were obtained. The values calculated by the authors of the present review from the tabulated data are quoted without references. When several experimental studies have been made, the $E_S$ were evaluated from the most reliable data and are given in the corresponding row.

The error of the initial experimental quantities is quoted after the original communications. The error of the calculated quantities is given in those cases where they have been obtained from reliable experimental data accompanied by the authors' estimate of the error.

If the experimental data referred to a temperature other than 298 K, we recalculated them for the standard temperature.

*The number of members in the ring.

**Here and henceforth the numerals in square brackets denote references (Ed.of Translation).

Indeed, the $E_S$ for five- and seven-membered rings are similar and the equilibrium yields of polymers also do not differ very greatly. On the other hand, the transposition of the formals with five and seven members in the ring can probably be accounted for by the effect of the entropy of polymerisation. It follows from general considerations that, with decrease of the number of members in the ring, the difference between the entropies of the linear polymer (calculated for the corresponding unit) and the monomer should diminish. The experimental entropies of polymerisation of lactams confirmed this. It has been shown that,[52] with decrease of the number of members in the ring from 8 to 5, $\Delta S$ gradually diminishes, changing sign at the same time. Whereas the entropy change is favourable for the polymerisation process in the case of eight- and seven-membered rings, in the case of five- and six-membered rings, it becomes unfavourable and the polymerisation reaction takes place by virtue of the enthalpy change or, in other words, the strain energy $E_S$. One can assume with

complete justification that the dependence of $\Delta S$ for polymerisation on $n$ has the character as for cyclic formals.

We may note that, although the thermochemistry of heterocyclic compounds has been investigated in order to elucidate and refine our knowledge about their capacity for polymerisation, the measurement of strain energies is of wider importance. It is to be expected that, for comparatively high values of $E_S$, other reactions involving the opening of the ring and the formation of straight-chain products will also take place more readily. Many instances of different reactivities of substances as a function of ring size are known for heterocyclic compounds. Thus tetrahydrofuran is more reactive than tetrahydropyran; five-membered glucosides are more reactive than six-membered glucosides and five-membered γ-monosaccharides are so unstable, in contrast to the six-membered compounds, that they have not even been isolated in a free state.[26]

The enthalpies of combustion of several monosaccharides as well as certain other oxygen-containing cyclic compounds are listed in Table 3. The contribution to the $\Delta H_C^\circ$ by the -O- group, found as the difference between $\Delta H_C^\circ$ for di-*n*-butyl ether (Table 3) and *n*-octane [50] and amounting to 125.0 kJ mol$^{-1}$ in the gaseous state, was used to calculate the $E_S$ for cyclic oxygen-containing compounds. Comparison of data obtained for the simplest oxygen-containing heterocycles (tetrahydrofuran and tetrahydropyran) shows that the strain energy of the six-membered ring is close to zero, while the strain energy of the five-membered ring is ~24 kJ mol$^{-1}$. Similar results are quoted above for cyclic formals and lactams.

Table 3. The enthalpies of combustion and evaporation and the strain energies of certain oxygen-containing cyclic compounds at 298 K (in kJ mol$^{-1}$).

| Substance | *n* | $-\Delta H_C^0$ | $\Delta H_v^\circ$ | $-\Delta H_C^\circ$ (gas) | $E_S$ |
|---|---|---|---|---|---|
| Tetrahydrofuran (l) | 5 | 2501.2±0.4 [26] | 32.5±0.2 [63] | 2533.7±0.5 | 24.2 |
| | 5 | — | — | 2533.2±0.7 [64] | — |
| Tetrahydropyran (l) | 6 | 3137.6±0.8 [26] | 34.9±0.8 [65] | 3172.5±1.1 | 4.3 |
| | 6 | — | — | 3173.3±1.0 [64] | — |
| 2-Methoxytetrahydropyran (l) | 6 | 3633.8±1.2 [26] | — | — | — |
| α-D-Xylose (s) | 6 | 2338.9±0.8 [26] | — | — | — |
| α-D-Glucose (s) | 6 | 2803.2±0.6 [26] | — | — | — |
| | 6 | 2802.7±0.6 [50] | — | — | — |
| Methyl β-D-glucofuranoside (l) | 5 | 3552.6±0.8 [26] | — | — | (22.0)* |
| Methyl β-D-glucopyranoside (s) | 6 | 3517.9±0.4 [26] | — | — | — |
| Methyl α-D-glucopyranoside (s) | 6 | 3522.1±0.8 [26] | — | — | — |
| Di-n-butyl ether (l) | — | 5343.4±3.3 [26] | 44.4 [66] | 5387.8 | — |
| | — | 5342.6±0.9 [67] | 44.4 [66] | 5387.0 | — |

*Here and in the subsequent Tables the quantities calculated from insufficiently reliable data or calculated using approximate methods are enclosed in round brackets.

Analysis of the $\Delta H_C^\circ$ for carbohydrates and other oxygen-containing cyclic compounds led to the conclusion[26,68] that the relations characteristic of compounds of other classes are typical also for them. Thus the simplest additive calculation of thermodynamic quantities is entirely feasible for carbohydrates whose molecules contain a large number of polar functional groups. On this basis, the authors[26,68] estimated the $E_S$ for the five-membered methyl β-D-glucofuranoside by comparing its enthalpy of combustion with the $\Delta H_C^\circ$ for the six-membered methyl β-D-glucopyranoside assuming that $E_S \approx 0$ for the latter, by analogy with other six-membered rings. Since the $\Delta H_V^\circ$ for these substances are unknown, the estimate could be carried out only for the liquid state. Table 3 shows that the $\Delta H_C^\circ$ for these two glucosides differ by ~30 kJ mol$^{-1}$ despite their overall formulae being identical. Having taken into account the enthalpy of fusion of methyl α-D-glucopyranoside, the authors[26,68] obtained the strain energy of methyl β-D-glucofuranoside, amounting to ~22 kJ mol$^{-1}$, which is very close to $E_S$ for tetrahydrofuran and other five-membered rings. The higher reactivity of five-membered rings can apparently be also explained by the appreciable strain energy. The polymerisation of γ-monosaccharides as well as other low-molecular-weight cyclic compounds, which is possible by virtue of the high $E_S$, probably plays an appreciable role in the biosynthesis of higher carbohydrates in nature.

The study of the mutual influence of the amino-groups and oxygen-containing groups is closely related to the investigation of cyclic lactams. Measurements have been made[69] of the $\Delta H_C^\circ$ for aliphatic aminoacids and the interaction energies of the amino- and carboxy-groups, amounting to ~13 kJ mol$^{-1}$, have been estimated. The similarity of the $\Delta H_C^\circ$ for different aminocaproic acids with different positions of the amino-group is evidence of the approximate constancy of the energy of this interaction.

## IV. ENTHALPIES OF COMBUSTION OF BRANCHED ALKANES

The measurement of the enthalpies of combustion and formation of branched alkanes made it possible to estimate the contribution of the interaction of hydrogen atoms in close proximity, for example in the methyl groups at quaternary carbon atoms separated by one methylene group. This interaction was not taken into account by the constants of the additive scheme proposed for the calculation of the enthalpies of formation of hydrocarbons.[70] On the other hand, the average difference between the experimental and calculated[70] $\Delta H_C^\circ$ amounted to ±2 kJ mol$^{-1}$; in three cases, namely for 2,2,4-trimethylpentane, 2,2,3,4-tetramethylpentane, and 2,2,4,4-tetramethylpentane, discrepancies between the calculated and experimental values exceeding the experimental error were noted. A prediction has been made[70,71] that the interaction of the methyl groups in such substances may be significant. It has been noted[72] that the distance between the closest hydrogen atoms of the $CH_3$ groups in the 2- and 4-positions in 2,2,4,4-tetramethylpentane, calculated on the assumption of a "staggered" configuration, is 0.0729 nm, whereas, for example, in the methyl group it is 0.1786 nm. Such an anomalous approach of the hydrogen atoms should alter the internal energy, by an amount which remains considerable even if one takes into account the fact that it is reduced somewhat owing to the rotation of methyl groups, which distort the valence angles.

The energy of interaction has been determined quantitatively[73] by measuring the enthalpies of combustion of several branched alkanes. The validity of the determination of the $\Delta H_C^\circ$ for 2,2,4,4-tetramethylpentane [73] has been confirmed by the satisfactory agreement of this value with the results of Johnson et al.[74]. The data obtained were used to calculate the correction which must be taken included in the calculation, by an additive scheme taking into account the first interaction sphere,[70] of the $\Delta H_C^\circ$ for all alkanes containing hydrogen atoms in close proximity, i.e. the C(3)–C–C(4) or C(4)–C–C(4) fragments. Taking into account this correction, the enthalpies of combustion of branched alkanes at 298 K can be calculated from the formula[72]

$$\Delta H_c^0 \text{ (kJ mol}^{-1}) = \sum_{i=1}^{4}\sum_{j=i}^{4} n_{ij} H_{ij(c)} - 10.13k$$

where $k = 1$ for each C(3)–C–C(4) fragment and $k = 2$ for each C(4)–C–C(4) fragment; $j \neq 1$.

## V. THERMOCHEMISTRY OF CYCLIC HYDROCARBONS AND THEIR DERIVATIVES

In recent years much attention has been devoted in the thermochemistry of organic compounds to the study of cyclic hydrocarbons and their simplest derivatives. The special interest in the thermochemistry of cyclic compounds is determined mainly by two causes: (1) the high specific combustion energy of a number of substances belonging to this class; (2) the specific thermochemical relations which are characteristic of cyclic compounds but have so far been little investigated.

Among these substances, compounds with small rings (three- and four-membered) are especially interesting because of their unusual structural and chemical features. For this reason special attention has been devoted to them in this review. We shall not dwell on the analysis of the thermochemical data for other monocyclanes and their derivatives, since they are few in number and in addition are well known.[50,75]

Table 4. The enthalpies of combustion, formation, and evaporation (sublimation) and strain energies of cyclopropane, cyclopropene, and their substituted derivatives at 298 K (in kJ mol$^{-1}$).

| Substance | $-\Delta H_c^0$ | $\Delta H_f^0$ (l or s) | $\Delta H_v^0$ or $\Delta H_s^0$ | $\Delta H_f^0$ (g) | $E_s$ |
|---|---|---|---|---|---|
| Cyclopropane (g) | 2091.3±0.5 [80] | — | — | 53.3±0.5 | 115.4 |
| Methylcyclopropane (l) | 2719.1±0.6 [81] | 1.7±0.6 | 22.6* | 24.3 | 115.8 |
| *cis*-1,2-Dimethylcyclopropane (l) | 3370.4±0.6 [81] | −26.3±0.6 | 28.0* | 1.7 | 122.7 |
| *trans*-1,2-Dimethylcyclopropane (l) | 3366.0±0.8 [81] | −30.7±0.8 | 26.9* | −3.8 | 117.2 |
| 1,1-Dimethylcyclopropane (l) | 3363.4±0.7 [82] | −33.3±0.7 | 25.1±0.8 [83] | −8.2±1.2 | 115.5 |
| 1,1,2-Trimethylcyclopropane (l) | 3979.9±0.8 [81] | −96.2±0.8 | 30.5* | −65.7 | 87.4 |
| 1,1,2,2-Tetramethylcyclopropane (l) | 4635.6±0.8 [81] | −119.8±0.8 | 33.6* | −86.2 | 99.0 |
| Ethylcyclopropane (l) | 3371.9±0.8 [81] | −24.8±0.8 | 28.2* | 3.4 | 115.7 |
| | 3384.0 [84] | — | — | — | — |
| 1-Ethyl-2,2-Dimethylcyclopropane (l) | 4665.2±0.8 [85] | −90.2±0.8 | 33.5* | −56.7 | 117.1 |
| 2,2-Dimethyl-1-propylcyclopropane (l) | 5318.7±1.7 [85] | −116.0±1.7 | 38.9* | −77.1 | 117.4 |
| Hexylcyclopropane (l) | 5513.7** [84] | −314.5 | — | — | — |
| 1-Hexyl-2,2-dimethylcyclopropane (l) | 7279.0±1.7 [85] | −193.0±1.7 | 51.6* | −141.4 | 115.2 |
| *cis*-1,2-Diethylcyclopropane (l) | 4675.5±1.3 [86] | −79.9±1.3 | 35.4±0.8 [86] | −44.5±1.5 | 117.9 |
| *trans*-1,2-Diethylcyclopropane (l) | 4672.1±2.1 [86] | −83.3±1.2 | 34.3±0.8 [86] | −49.0±2.3 | 113.4 |
| *cis*-1,2-Dimethyl-3,3-dichlorocyclopropane (l) | 3071.3±0.9 [87] | −86.9±0.9 | (39.5)*** | −47.4 | (134.4) |
| *trans*-1,2-Dimethyl-3,3-dichlorocyclopropane (l) | 3067.9±1.1 [87] | −90.2±1.1 | (39.5)*** | −50.7 | (131.1) |
| Bicyclopropyl (l) | 3886.0±3.0 [88] | 95.9±3.0 | 33.5±1.2 [88] | 129.4±3.2 | 228.1 |
| Vinylcyclopropane (l) | 3213.3±0.8 [89] | 102.5±0.8 | 28.7±1.3 [89] | 131.2±1.5 | 116.7 |
| | 3233.4 [84] | 122.6 | — | — | — |
| | — | 98.7 [90] | — | — | — |
| Isopropenylcyclopropane (l) | 3851.4±1.3 [91] | 61.2±1.3 | 28.4±0.2 [91] | 89.6±1.3 | 109.9 |
| 3-Cyclopropylbuta-1,2-diene (l) | 4379.5±1.7 [91] | 195.8±1.7 | 37.7* | 233.5 | 110.7 |
| Ethynylcyclopropane (l) | 3086.1±0.8 [89] | 261.1±0.8 | 30.9±1.5 [89] | 292.0±1.7 | 112.7 |
| Methylenecyclopropane (g) | 2632.1±1.8 [92] | — | — | 200.5±1.8 | 170.9 |
| Trimethylenecyclopropane (g) | — | — | — | 395.8 [93] | (205.4) |
| 1,1-Diethynylcyclopropane (l) | 4113.0±0.8 [91] | 500.9±0.8 | 37.6* | 538.5 | 113.5 |
| Dicyclopropyldiacetylene (l) | 5869.5±1.7**** | 505.2±1.7 | 58.2±1.0**** | 563.4±2.0 | 183.0 |
| Phenylcyclopropane (l) | 5071.0±0.9 [94] | 100.3±0.9 | 50.22±0.10 [95] | 150.5±0.9 | 103.9 |
| | 5076.4 [84] | 105.7 | — | — | — |
| 1,1-Diphenylcyclopropane (l) | 8088.9±3.3 [94] | 185.4±3.3 | 65.5* | 250.9 | — |
| *cis*-1,2-Diphenylcyclopropane (l) | 8082.2±0.8 [94] | 178.7±2.1 | — | — | — |
| *trans*-1,2-Diphenylcyclopropane (l) | 8059.7±2.5 [94] | 166.2±3.2 | 66.6* | 232.8 | 77.4 |
| 1-Cyclopropyl-2-methylbenzene (l) | 5725.4±0.8 [96] | 75.4±1.2 | 52.0* | 127.4 | 113.8 |
| 1-Cyclopropyl-2,4-dimethylbenzene (l) | 6366.0±1.3 [96] | 36.4±1.3 | 55.0* | 91.4 | 110.7 |
| 1-Cyclopropyl-2,4,6-trimethylbenzene (l) | 7014.1±2.1 [96] | 5.4±2.1 | 58.3* | 63.7 | 115.9 |
| 1-Cyclopropyl-4-isopropylbenzene (l) | 7022.8±1.7 [96] | 14.2±1.7 | — | — | — |
| Cyclopropyl methyl ketone (l) | 2956.2±1.0 [97] | 154.7±1.0 | 39.41±0.09 [98] | −115.3±1.0 | 106.3 |
| *cis*-2-Carboxy-1-phenylcyclopropane (s) | 5043.4±2.1 [99] | −320.9±2.1 | 103.3±0.6 [91] | −217.6±2.2 | 115.1 |
| *trans*-2-Carboxy-1-phenylcyclopropane (s) | 5032.1±2.1 [99] | −332.1±2.1 | 104.8±0.2 [91] | −227.4±2.1 | 101.2 |
| *cis*-2-Ethoxycarbonyl-1-phenylcyclopropane (l) | 6423.1±1.2 [91] | −299.9±1.2 | 70.7±0.6 [91] | −229.2±1.3 | 101.7 |
| *trans*-2-Ethoxycarbonyl-1-phenylcyclopropane (s) | 6385.8±1.2 [91] | −337.2±1.2 | 96.9±0.4 [91] | −240.3±1.3 | 90.6 |
| Cyclopropene (g) | 2029.2±2.5 [50] | — | — | 277.1±2.5 | 225.2 |
| Methylcyclopropene (g) | 2675.1±1.1 [92] | — | — | 243.6±1.1 | 224.5 |
| 1,3,3-Trimethylcyclopropene (l) | 3927.9±0.8 [91] | 137.7±0.8 | 26.8±1.7 [91] | 164.5±1.9 | 199.8 |
| Spiropentane (l) | 3296.0±0.7 [100] | — | — | 185.1±0.7 | 265.8 |
| | 3258.4±1.3 [101] | 147.5±1.3 | 27.53±0.04 [102] | 175.0±1.3 | — |

*The enthalpy of evaporation was calculated from the Klages formula.[103]

**The value of $\Delta H_c^\circ$ for hexylcyclopropane, given by Fierens and Nasielski[84] and also quoted by Pedley and Rylance,[50] deviates sharply from the series of $\Delta H_c^\circ$ for other substituted cyclopropanes.

***The $\Delta H_v^\circ$ were estimated from the group contributions quoted by Lebedev and Miroshnichenko.[83] The contribution of the three-membered ring to $\Delta H_v^\circ$, amounting to 3.3 kJ mol$^{-1}$, was obtained from a comparison of the experimental and calculated $\Delta H_v^\circ$ for cyclopropane and 1,1-dimethylcyclopropane.

****Determined by S.M.Pimenova in the Laboratory of Thermochemistry at Moscow State University.

### 1. Three- and Four-Membered Rings

The variation of the strain energy of the three-membered ring in substituted cyclopropanes and cyclopropenes is illustrated in Table 4. The nature of the bonds in cyclopropane and the interaction of the ring with substituents have been the subject of numerous theoretical studies.[76-79] For example, the interaction of the three-membered ring with various substituents, in the first place π-donors and π-acceptors, has been examined[79] within the framework of perturbation methods using molecular orbitals. The effect of the interaction was estimated[79] mainly from the change in the geometry of the ring. However, as can be seen from the same investigation, this criterion is by no means always sufficiently sensitive.

Thermochemical data for cyclopropane derivatives are fairly numerous and are of undoubted interest. The results of the measurements of the $\Delta H_c^\circ$ and $E_S$ for substituted cyclopropanes, presented in Table 4, show that the interaction of the substituent with the three-membered ring is complex and that the effect of the stabilisation (or destabilisation) of the ring does not always agree with the postulated effect. The substitution of hydrogen by one or two methyl groups gives rise to a relatively small effect. An appreciable decrease of $E_S$ has been observed for 1,1,2-trimethylcyclopropane and 1,1,2,2-tetramethylcyclopropane, going far beyond the limits of experimental error. However, this effect has not been noted for 2-n-alkyl-1,1-dimethylcyclopropanes. It has been shown[85] that the presence of the strained three-membered ring in the molecules of compounds of this series does not affect the bond energies in the side chain; this enabled the authors[85] to put forward a formula for the calculation of the $\Delta H_c^\circ$ for liquid 1-n-alkyl-2,2-dimethylcyclopropanes, starting with 1-ethyl-2,2-dimethylcyclopropane:

$$-\Delta H_c^0 \text{ (liq.) (kJ mol}^{-1}) = 4665.2 + (n-7)\,653.7,$$

where $n \geq 7$ is the number of carbon atoms in the molecule.

The strain energies of the *cis*- and *trans*-isomers of 3,3-dichloro-1,2-dimethylcyclopropane proved to be much greater than the $E_S$ for their hydrocarbon analogues. This conclusion must be regarded as preliminary, since the $\Delta H_v^\circ$ for these compounds are approximate estimates and the energy contribution of the $C-(Cl)_2(C)_2$ group (taken from Benson et al.[40]) used in the calculation of $\Delta H_f^\circ$(gas) for the hypothetical unstrained compound is not entirely reliable.

The introduction of an exocyclic double bond appreciably increases the strain energy of the ring, which can be seen in relation to methylenecyclopropane. In the calculation of $E_S$ for trimethylenecyclopropane it was assumed that the contribution of the $C_d-(C_d)_2$ group to $\Delta H_f^\circ$ is equal to the contribution of the $C_d-(C_d)(C)$ group; furthermore, the accuracy of the measurement of $\Delta H_f^\circ$(gas) is low. This makes it necessary to regard the result of the calculation of $E_S$ as approximate. However, the appreciable increase of $E_S$ in this case too can be hardly open to doubt (see Table 4). On the other hand, the strain energies of alkenyl- and alkynyl-cyclopropanes, in which the double (or triple) bond is separated from the ring by a single bond, are close to the $E_S$ for cyclopropane; for the majority of compounds, the difference is within the limits of the experimental error. This indicates the absence in most cases of an appreciable effect of the conjugation of the cyclopropane ring. However, there are also exceptions: the decrease of $E_S$ in cyclopropyl methyl ketone greatly exceeds the experimental error, while the strain energy of dicyclopropyldiacetylene calculated for a single ring is only 91.5 kJ mol$^{-1}$. The conjugation of the triple bonds probably plays a major role in the latter case.

When an endocyclic double bond is introduced, the strain energy of the three-membered ring increases even more than that after the introduction of the exocyclic bond. The same behaviour has been observed for methylcyclopropenes as for methylcyclopropanes: the $E_S$ for methylcyclopropene hardly differs from that for cyclopropene itself and the $E_S$ for 1,3,3-trimethylcyclopropene is significantly lower.

Phenylcyclopropanes have an even lower strain energy compared with the unsubstituted cyclopropane. For phenylcyclopropanes and 1,1-diphenylcyclopropanes, this decrease is approximately the same. The effect of the interaction of the phenyl group with the three-membered ring in 1,2-diphenylcyclopropanes depends on their relative positions: for the *trans*-isomer, $E_S$ is appreciably lower than for the *cis*-isomer. It is of interest that this feature is retained also in oxygen-containing phenyl-substituted derivatives: in phenylcyclopropanoic acids and their ethyl esters.

Comparatively few experimental enthalpies of combustion and strain energies are available for cyclobutane and cyclobutene derivatives (Table 5). So far as can be judged from the few reliable data, features similar to those noted above for cyclopropane and cyclopropene derivatives are characteristic of these compounds. Thus the strain energies of the alkyl-substituted derivatives differ little from the $E_S$ for cyclobutane. When a double bond is introduced, $E_S$ increases but the change in the $E_S$ for the four-membered ring is much smaller than for the three-membered ring.

Table 5. The enthalpies of combustion, formation, and evaporation and the strain energies of cyclobutane, cyclobutene, and their substituted derivatives at 298 K (in kJ mol$^{-1}$).

| Substance | $-\Delta H_c^0$ (l) | $\Delta H_f^0$ (l) | $\Delta H_v^0$ | $\Delta H_f^0$(g) | $E_S$ |
|---|---|---|---|---|---|
| Cyclobutane (l) | 2721.1±0.5 [104, 105] | 3.7±0.5 | 24.64±0.04 [106] | 28.4±0.5 | 111.2 |
| Methylcyclobutane (l) | 3352.2±1.3* [101] | −44.5±1.3 | — | — | — |
| Ethylcyclobutane (l) | 4017.1±0.7 [82] | −58.9±0.7 | 32.6±0.8 [82] | −26.3±1.1 | 106.7 |
| | — | — | 31.24±0.03 [98] | — | — |
| Bicyclo[1.1.0]-butane (g) | 2648.7±0.8 [92] | — | — | 217.2±0.8 | 274.5 |
| Isopropenylcyclobutane (l) | 4489.4±2.1** | 19.9±2.1 | — | — | — |
| *trans*-1,2-Divinylcyclo-butane (l) | 4990.8±1.6 [91] | 127.7±1.9 | 38.7±0.6 [91] | 166.4±2.0 | 95.9 |
| | 4964.3±3.3 [107] | 101.2±3.5 | — | — | — |
| 1-Vinylbicyclo-[1.1.0] butane (l) | 3725.8±5.4** | 221.3±5.4 | — | — | — |
| Isobutylcyclobutane (l) | 5317.4±1.7** | −117.3±1.7 | 41.1*** | −76.2 | 106.9 |
| Cyclobutene (g) | 2588.2±1.5 [92] | — | — | 156.7±1.5 | 124.7 |
| Methylenecyclobutane (l) | 3204.7±0.5 [82] | 93.9±0.5 | 27.7±0.4 [82] | 121.6±0.7 | — |
| | 3206.0±0.6 [109] | 95.1±0.6 | 23.9 [109] | 124.4±0.8 | 115.5 |

*The value of $\Delta H_c^\circ$ for methylcyclobutane appears to be doubtful.

**Determined by L.P.Timofeeva and L.V.Kulakova in the Laboratory of Thermochemistry at Moscow State University.

***Calculated from the Klages formula.[103]

### 2. Bicyclic Hydrocarbons with Separated Rings and Spirans

Table 6 presents the enthalpies of combustion and formation and the strain energies for bicyclic hydrocarbons in which two rings are separated by one or two σ-bonds and also for spirans. As was to be expected, the $E_S$ for the

individual rings in bicyclanes without a common carbon atom hardly differ from the $E_S$ for the corresponding monocyclanes. Thus the strain energy of one three-membered ring in bicyclopropyl is equal to the $E_S$ for cyclopropane within the limits of experimental error. The same feature has been observed also for other bicyclanes with analogous structures. It has been shown[111] that the difference between the enthalpies of combustion of a bicyclane and the corresponding monocyclanes in the liquid state is constant in all the known instances and amounts to $251.5 \pm 1.6$ kJ mol$^{-1}$. Thus the enthalpies of combustion of liquid bicyclanes in the molecules of which the rings are separated by one σ-bond can be calculated from the formula

$$\Delta H_c^0(\text{liq.})\ (\text{kJ mol}^{-1}) = [\Delta H_c^0(\text{liq.})]' + [\Delta H_c^0(\text{liq.})]'' + 251.5,$$

where $[\Delta H_C^\circ(\text{liq.})]'$ and $[\Delta H_C^\circ(\text{liq.})]''$ are the enthalpies of combustion of the corresponding monocyclanes.[11]

The difference between the enthalpies of combustion of dicyclopentylmethane and bicyclopentyl is −649.8 kJ mol$^{-1}$ according to Kozina et al.[11] Using this value and the data quoted above, it is possible to calculate approximately the $\Delta H_C^\circ$ for bicyclanes, in the molecules of which the rings are separated by the $-CH_2-$ group, from the formula

$$\Delta H_c^0(\text{liq.})\ (\text{kJ mol}^{-1}) = [\Delta H_c^0(\text{liq.})]' + [\Delta H_c^0(\text{liq.})]'' - 398.3,$$

where, as in the previous formula, $[\Delta H_C^\circ(\text{liq.})]'$ and $[\Delta H_C^\circ(\text{liq.})]''$ are the enthalpies of combustion of the corresponding monocyclanes. Presumably the interaction between the rings does not affect the thermodynamic quantities also in those cases where the number of rings separated by σ-bonds is greater than two.

Table 6. The enthalpies of combustion, formation, and evaporation and the strain energies of spiro-hydrocarbons and certain bicyclic hydrocarbons at 298 K (in kJ mol$^{-1}$).

| Substance | $-\Delta H_c^0$ | $\Delta H_f^0$ (l) | $\Delta H_v^0$ | $\Delta H_f^0$ (g) | $E_S$ |
|---|---|---|---|---|---|
| Bicyclopropyl (l) | 3886.0±3.3 [88] | 95.8±3.3 | 33.5±1.3 [88] | 129.3±3.6 | 228.0 |
| Bicyclopentyl (l) | 6332.5±2.9 [11] | −175.1±3.2 | 51.0* | −124.1 | — |
| Dicyclopentylmethane (l) | 6328.3±0.8 [110] | −179.3±0.8 | — | −128.3 | 53.3 |
| Cyclopentylcyclohexane (l) | 6981.8±2.1 [11] | −205.1±2.1 | 52.7* | −152.4 | 49.9 |
| Bicyclohexyl (l) | 6956.7 [11] | −230.2 | 55.2* | −175.0 | 27.3 |
| Cyclopentylcycloheptane (l) | 7593.0±0.8 [110] | −273.3±0.8 | — | — | — |
| Bicycloheptyl (l) | 7640.0±3.8 [11] | −226.3±3.8 | 58.6* | −167.7 | 55.3 |
| Spiropentane (g) | 8940.0±2.5 [11] | −285.0±2.5 | 63.3* | −221.7 | 42.7 |
| Spiropentane (l) | 3296.0±0.7 [100] | — | — | 185.1±0.7 | 265.8 |
| Spiro[4,4]nonane (l) | 3258.4±1.3 [101] | 147.5±1.3 | 27.53±0.04 [102] | 175.0±1.3 | — |
| Spiro[4,5]decane (l) | 5684.4±1.3 [111] | −143.8±1.3 | 46.2* | −97.6 | 67.0 |
| Spiro[5,5]undecane (l) | 6307.4±1.3 [111] | −200.2±1.3 | 54.9±0.1 [113] | −145.3±1.3 | 39.0 |
| Spiro[5,6]dodecane (l) | 6307.5±2.0 [112] | −200.0±2.1 | 54.9±0.1 [113] | −145.1±2.1 | — |
| | 6938.7±2.1 [111] | −248.2±2.1 | 56.1±0.1 [113] | −192.1±2.1 | 12.9 |
| | 6942.4±2.8 [112] | −244.5±3.0 | 56.1±0.1 [113] | −188.4±3.0 | — |
| | 7613.2±0.8 [111] | −253.0±0.8 | 57.3* | −195.7 | 30.0 |
| | 7613.8±2.3 [112] | −252.4±2.5 | 57.3* | −195.1 | — |

*Calculated from the Klages formula.[103]

On the other hand, the strain energies of spiro-hydrocarbons are greater than some of the $E_S$ for the individual rings. For example, the strain energy of one three-membered ring in spiropentane is 132.8 kJ mol$^{-1}$, which exceeds by ~17 kJ mol$^{-1}$ the strain energy of cyclopropane. The increase of $E_S$ relative to the additive value has been observed also for other spiro-hydrocarbons, although the effect for these substances is smaller than for spiropentane (Table 6).

It has been shown[111] that, when the strain energies of individual rings in spiro-hydrocarbons are assumed to be equal to the values of $E_S$ for the corresponding monocyclanes, then the contribution introduced by the quaternary carbon atom to $\Delta H_C^\circ$ and $\Delta H_f^\circ$ is found to be constant for all four spirans investigated by Kozina et al.[111] This contribution naturally differs from that adopted by Benson et al.[40] since account was taken of the thermochemical characteristics of spirans in its calculation. By taking into account the data of Subach and Zvolinski,[112] the following formulae have been obtained for the approximate calculation of $\Delta H_C^\circ$ and $\Delta H_f^\circ$ for spirans (apart from those containing three- and four-membered rings):

$$-\Delta H_c^0(\text{gas})\ (\text{kJ mol}^{-1}) = 406.2 + 658.63n + \Sigma E_s,$$
$$\Delta H_f^0(\text{gas})\ (\text{kJ mol}^{-1}) = 12.8 - 20.71n + \Sigma E_s,$$

where $n$ is the number of $-CH_2-$ groups and $E_S$ the strain energies of the constituent rings of the given molecule according to Benson et al.[40]

### 3. Bridged and Condensed Bicyclic Hydrocarbons

The study of bicyclic hydrocarbons and their simplest derivatives has aroused much interest in recent years. The experimental measurement of the standard enthalpies of formation and of the strain energies calculated from them occupies an important place in such research. The special interest in the strain energies of these compounds is determined, in particular, by the fact that an increase in the rigidity of the molecular skeleton on passing from monocyclic to bicyclic and polycyclic compounds entails a change in the geometry of the individual rings, which greatly affects $E_S$. Thus, measurement of $E_S$ in combination with conformational analysis and electron diffraction and spectroscopic studies makes it possible to investigate the nature of the strain.[114-117] On the other hand, there remains the problem of the empirical study of $\Delta H_f^\circ$ and $E_S$ in order to investigate the influence of substituents, the introduction of a double bond, etc. on the latter with the aim of establishing the thermochemical relations for predicting the thermodynamic properties of compounds which have not been investigated. This Section deals with the results of thermochemical studies on compounds of two classes: bridged bicyclic hydrocarbons and their derivatives, i.e. [*n.m.k*]bicyclic compounds, and condensed bicyclic compounds, i.e. [*n.m.*0]-bicyclic compounds.

The thermochemical data for bridged bicyclic hydrocarbons and their simplest derivatives are presented in Table 7. The greatest number of experimental data are available for derivatives of bicyclo[2.2.1]heptane (norbornane). Table 7 shows that the strain energies of norbornane derivatives depend greatly not only on the number but also on the positions of the substituents. Even when hydrogen atoms are replaced by one or two methyl groups, $E_S$ varies from ~55 to ~80 kJ mol$^{-1}$. The introduction of the $CH_3$ group in the 2-position or even two $CH_3$ groups in the 2- and 3-positions, which are most remote from the "bridge" has comparatively little effect on the strain energy. On the other hand, $E_S$ for 1-methylnorbornane is lower by almost 10 kJ mol$^{-1}$ than for the unsubstituted norbornane. The introduction of two methyl groups at tertiary carbon atoms, i.e. in the 1- and 4-positions stabilises the molecule to an even greater extent. On the other hand, $E_S$ for 7,7-dimethylnorbornane is ~10 kJ mol$^{-1}$ higher than for norbornane.

**Table 7.** The enthalpies of combustion, formation, and evaporation (sublimation) and the strain energies of bridged bicyclic hydrocarbons and their derivatives at 298 K (in kJ $mol^{-1}$).

| No. | Substance | $-\Delta H_c^0$ | $\Delta H_f^0$ (l or s) | $\Delta H_v^0$ or $\Delta H_s^0$ | $\Delta H_f^0$ (g) | $E_s$ |
|---|---|---|---|---|---|---|
| 1 | Bicyclo[2.2.1]heptane (norbornane) (s) | 4377.5±2.2 [118] | −92.1±2.2 | 40.1±0.8 [119] | −52.0±2.3 | 67.4 |
| | | 4367.5±3.3 [120] | −102.0±3.3 | 40.4±0.8 [120] | −61.6±3.4 | — |
| 2 | *exo*-2-Methylnorbornane (l) | 5026.4±1.1 [121] | −122.5±1.1 | 41.8* | −80.7 | 68.2 |
| 3 | *endo*-2-Methylnorbornane (l) | 5026.8±1.2 [121] | −122.1±1.2 | 41.0* | −81.1 | 67.8 |
| 4 | 1-Methylnorbornane (l) | 5018.0±1.0 [121] | −131.0±1.0 | 38.1±0.2 [122] | −92.8±1.0 | 58.8 |
| 5 | 1,4-Dimethylnorbornane (l) | 5660.8±1.3 [123] | −167.5±1.3 | 38.9±0.4 [124] | −128.6±1.4 | 55.1 |
| 6 | *trans*-2,3-Dimethylnorbornane (l) | 5678.0±1.9 [123] | −150.3±1.9 | 42.3±0.5 [124] | −108.0±2.0 | 70.3 |
| 7 | 7,7-Dimethylnorbornane (s) | 5680.0±1.5 [125] | −148.2±1.5 | 47.0±1.0 [125] | −101.2±1.8 | 79.8 |
| 8 | 2-Ethylnorbornane (l) (mixture of isomers: 36% *exo*-, 64% *endo*-) | 5688.0±1.8 [125] | −140.3±1.8 | — | — | — |
| 9 | Bicyclo[2.2.1]hept-2-ene (norbornene) (s) | 4213.5±1.7 [126] | 29.7±1.7 | 33.6±0.1 [126] | 63.3±1.7 | — |
| | | 4225.1±1.3 [127] | 41.4±1.3 | 38.7±0.4 [127] | 80.1±1.4 | 82.7 |
| | | 4237.2±3.2 [120] | 53.5±3.2 | 37.7±0.8 [120] | 91.2±3.3 | — |
| | | — | — | — | 89.5±2.6 [128] | — |
| | | — | — | — | 86.6** [130] | — |
| 10 | 2-Methylenenorbornane (l) | 4859.0±1.7 [46] | −4.1±1.7 | 39.4±0.1 [122] | 35.3±1.7 | 63.8 |
| 11 | 7-Methylenenorbornane (l) | 4882.7±2.1 [129] | 19.7±2.1 | 40.7* | 60.4 | 86.2 |
| 12 | 2-Methylnorbornene (l) | 4867.5±1.7 [123] | 4.4±1.7 | 39.4±0.2 [122] | 43.8±1.7 | 82.3 |
| 13 | 6-Methylnorbornene (l) (mixture of isomers: 44% *exo*-, 56% *endo*-) | 4878.9±1.2 [46] | 15.8±1.2 | — | — | — |
| 14 | Bicyclo[2.2.1]hepta-2,5-diene (s) | 4076.7±1.0 [126] | 178.7±1.0 | 32.9±0.1 [126] | 211.7±1.0 | — |
| | | — | — | — | 233.0 [130]** | — |
| | | 4111.7±3.0 [120] | 213.8±3.0 | 33.8±0.8 [120] | 247.6±3.2 | — |
| | | — | — | — | 240.2±2.8 [128] | 129.5 |
| 15 | *trans*-5-Ethylidenebicyclo[2.2.1]hept-2-ene (l) | 5358.5±1.5 [46] | 101.9±1.5 | 44.6±1.1 [124] | 146.5±1.9 | 90.6 |
| 16 | *cis*-5-Ethylidenebicyclo[2.2.1]hept-2-ene (l) | 5363.2±1.7 [46] | 106.6±1.7 | 44.5±0.5 [124] | 151.1±1.8 | 95.2 |
| 17 | 5-Vinylbicyclo[2.2.1]hept-2-ene (l) (mixture of isomers: 35% *exo*-, 65% *endo*-) | 5371.7±1.4 [46] | 115.1±1.4 | — | — | — |
| 18 | 2,2-Dimethyl-3-methylenenorbornane (s) | 6146.4±2.1 [129] | −75.3±2.1 | 46.9±0.5 [129] | −28.4±2.2 | 55.7 |
| 19 | Bicyclo[3.3.1]nonane (s) | 5650.1±0.8 [108] | −178.1±0.8 | 50.6±2.1 [108] | −127.5±2.3 | 33.4 |
| 20 | Bicyclo[3.3.1]non-2-ene (s) | 5445.1±1.3 [131] | −97.3±1.3 | 48.2±0.4 [132] | −49.1±1.4 | −4.1 |
| 21 | Bicyclo[4.2.1]non-3-ene (s) | 5496.3±0.9 [131] | −46.1±0.9 | 49.7±0.8 [132] | 3.6±1.2 | 54.2 |
| 22 | Bicyclo[2.2.1]heptan-7-one (s) | 4002.4±2.3 [133] | −181.3±2.3 | 47.3±2.1 [133] | −134.0±3.1 | 94.1 |
| 23 | Bicyclo[2.2.1]heptan-2-one (s) | 3967.1±2.7 [133] | −216.6±2.7 | 48.9±1.7 [133] | −167.7±3.2 | 60.2 |
| 24 | 1-Methylbicyclo[2.2.1]heptan-2-one (l) | 4611.1±2.5 [97] | −252.0±2.5 | 47.6±0.2 [122] | −204.4±2.5 | 52.5 |
| 25 | 1,7,7-Trimethylbicyclo[2.2.1]heptan-2-one (s) | 5902.5±2.5 [134] | −319.2±2.5 | 51.9±1.3 [134] | −267.3±2.9 | 64.4 |
| 26 | 7-Oxabicyclo[2.2.1]heptane (l) | 3566.3±1.5 [118] | −223.9±1.5 | 40.6* | −183.3 | 54.3 |
| 27 | *exo*-2-Methyl-7-oxabicyclo[2.2.1]heptane (l) | 4215.7±1.7 [118] | −253.8±1.7 | 42.7* | −211.1 | 56.0 |
| 28 | *endo*-2-Methyl-7-oxabicyclo[2.2.1]heptane (l) | 4219.3±1.6 [118] | −250.3±1.6 | 43.5* | −206.8 | 60.3 |
| 29 | *exo*-2-Cyanobicyclo[2.2.1]heptane (l) | 4739.8±1.3*** [135] | 19.7±1.3 | — | — | — |
| 30 | *endo*-2-Cyanobicyclo[2.2.1]heptane (s) | 4740.4±1.5 [135] | 20.3±1.5 | — | — | — |
| 31 | 2,3-Diazabicyclo[2.2.1]hept-2-ene (s) | 3262.9±2.6 [140] | 152.1±2.6 | 55.3±0.6 [140] | 207.4±2.7 | 64.4 |
| 32 | Bicyclo[2.2.2]octane (s) | 5001.9±0.8 [136] | −147.0±0.8 | 48.0±0.4 [137] | −99.0±1.0 | 41.2 |
| 33 | Bicyclo[2.2.2]oct-2-ene (s) | 4839.7±0.7 [136] | −23.4±0.7 | 43.8±0.4 [137] | 20.4±0.8 | 43.7 |
| | | — | — | — | 19.4 [130]** | — |
| 34 | 2-Methylenebicyclo[2.2.2]octane (l) | 5488.0±2.4 [138] | −54.4±2.4 | 45.2* | −9.2 | 38.2 |
| 35 | 2-Methylbicyclo[2.2.2]oct-2-ene (l) | 5480.4±2.1 [138] | −62.0±2.1 | 43.3±0.7 [139] | −18.7±2.2 | 30.5 |
| 36 | Bicyclo[3.2.2]non-6-ene (s) | 5490.9±2.1 [131] | −51.5±2.1 | 48.0±1.0 [132] | −3.5±2.3 | 41.5 |
| 37 | 1-Azabicyclo[2.2.2]octane (s) | 4557.4±1.2 [136] | −55.1±1.2 | 50.8±0.5 [137] | −4.3±1.3 | 46.5 |
| 38 | 1,4-Dimethyl-2,3-diazabicyclo[2.2.2]oct-2-ene (s) | 4883.5±4.4 [140] | 20.4±4.4 | 72.0±0.5 [140] | 92.4±4.4 | 42.3 |
| 39 | 3-Oxabicyclo[3.2.2]nonane (s) | 4873.3±0.8 [136] | −275.6±0.8 | 53.1±0.6 [137] | −222.5±1.0 | 43.6 |
| 40 | 3-Azabicyclo[3.2.2]nonane (s) | 5191.2±0.7*** [136] | −100.6±0.7 | 57.9±0.4 [137] | −42.7±0.8 | 46.8 |
| 41 | Bicyclo[3.3.2]decane (s) | 6343.4±7.1 [108] | −164.2±7.1 | 58.2±2.1 [108] | −106.0±7.4 | 75.6 |
| 42 | Bicyclo[3.3.3]undecane (s) | 7034.3±1.7 [141] | −152.6±1.7 | 63.6±0.8 [141] | −89.0±1.9 | 113.3 |

*Calculated from the Klages formula.[103]

**In the calculation of $\Delta H_f^\circ$ from the enthalpy of hydrogenation, the values of $\Delta H_f^\circ$ for the corresponding saturated compounds, taken from Pedley and Rylance,[50] were used here and henceforth.

***Recalculated by ourselves for 298 K.

The introduction of an endocyclic double bond appreciably increases $E_s$ but not to the extent observed for the three-membered ring. The influence of an exocyclic double bond depends on the position of the methylene group: the strain energy of 2-methylenenorbornane is a little lower and that of 7-methylenenorbornane is significantly higher than the $E_s$ for the initial molecule. $E_s$ is even greater for *cis*- and *trans*-ethylidenenorbornanes. The influence of the substitution of a hydrogen atom by the oxo-group is similar to the influence of the $=CH_2$ group: the oxo-group in the 7-position significantly increases while in the 2-position it slightly diminishes the strain energy. The introduction of the methyl group in the 1-position in the molecule of bicyclo[2.2.1]heptan-2-one, reduces $E_s$ still further, analogously to such substitution in norbornane. The replacement of the $-CH_2-$ group in the bridge by an ether oxygen atom entails some decrease of the $E_s$ for the 7-oxabicyclo[2.2.1]heptane molecule, in contrast to the three-membered ring, whose strain energy $E_s$ remains almost unaltered following such substitution.[40]

Bicyclo[2.2.2]octane is an interesting compound for the investigation of the nature of strain. Its molecule can be imagined as being made up of, as it were, two six-membered rings, but its strain energy proved to be unexpectedly extremely high, amounting to ~40 kJ $mol^{-1}$. It has been suggested[136] that this strain is mainly determined by the presence of three pairs of hydrogen atoms in the "eclipsed" conformation. The influence of the methyl substitution and also of exocyclic and endocyclic double bonds on the $E_s$ for bicyclo[2.2.2]octane is qualitatively similar to that noted above for norbornane derivatives, but is much weaker.

The marked dependence of $E_s$ on the structure of the molecule and on the position of the double bond is evident from the example of certain saturated hydrocarbons (Nos.1, 19, 41, and 42) and three bicyclononene isomers (Nos.20, 21, and 36, Table 7).

**Table 8.** The enthalpies of combustion, formation, and evaporation (sublimation) and the strain energies of condensed bicyclic hydrocarbons and their derivatives at 298 K (in kJ $mol^{-1}$).

| No. | Substance | $-\Delta H_c^0$ | $\Delta H_f^0$ (l or s) | $\Delta H_v^0$ or $\Delta H_s^0$ | $\Delta H_f^0$ (g) | $E_s$ |
|---|---|---|---|---|---|---|
| 1 | Bicyclo[1.1.0]butane (g) | 2648.7±0.8 [92] | — | — | 217.2±0.8 | 274.5 |
| 2 | Bicyclo[2.1.0]pentane (l) | 3241.6±1.3 [91] | 130.7±1.3 | 28.0±0.3 [124] | 158.7±1.3 | 236.7 |
| | | — | — | — | 152.3±1.7 [142] | — |
| 3 | Bicyclo[3.1.0]hexane (l) | 3795.3±2.1 [143] | 5.1±2.1 | 33.5±0.4 [143] | 38.6±2.1 | 137.3 |
| 4 | 1-Methylbicyclo[3.1.0]hexane (l) | 4436.4±1.2 [123] | −33.1±1.2 | 34.6±0.4 [124] | 1.5±1.3 | 132.4 |
| 5 | 1,3,5-Trimethylbicyclo[3.1.0]hexane (l) | 5726.2±2.1* | −102.0±2.1 | 41.5** | −60.5 | 131.9 |
| 6 | 5-Ethyl-1-methylbicyclo[3.1.0]hexane (l) | 5730.0±2.1* | −98.2±2.1 | 42.8** | −55.4 | 128.3 |
| 7 | Bicyclo[3.1.0]hex-3-ene (l) | 3625.0±2.9 [46] | 120.6±2.9 | — | — | — |
| 8 | Bicyclo[4.1.0]heptane (norcarane) (l) | 4442.3±1.2 [46] | −27.2±1.2 | 38.8±0.6 [124] | 11.6±1.3 | 131.0 |
| | | 4432.7±2.6 [143] | −36.8±2.6 | 38.1±0.8 [143] | 1.3±2.7 | — |
| 9 | 1-Methylnorcarane (l) | 5089.0±1.4 [123] | −59.9±1.4 | 39.5±0.6 [124] | −20.4±1.5 | 131.2 |
| 10a | *cis*-3,7,7-Trimethylnorcarane (carane) (l) | 6391.6±2.6 [144] | −116.0±2.6 | 47.1±1.2 [124] | −68.9±2.9 | 141.5 |
| 10b | *trans*-Carane (l) | 6389.1±2.5 [144] | −118.5±2.5 | 48.1±1.1 [124] | −70.4±2.7 | 140.0 |
| 11 | Bicyclo[4.1.0]hept-2-ene (l) | 4258.4±2.8* | 74.7±2.8 | 41.5±0.6 [124]*** | 116.2±3.0 | 119.8 |
| 12 | 3,7,7-Trimethylbicyclo[4.1.0]hept-2-ene (2-carene) (l) | 6199.1±2.3 [145] | −22.6±2.3 | 47.8 [146] | 25.2 | 125.2 |
| 13 | 3,7,7-Trimethylbicyclo[4.1.0]hept-3-ene (3-carene) (l) | 6192.1±1.8 [145] | −29.6±1.8 | 48.3±3.1 [146] | 18.7±3.6 | 119.7 |
| 14 | *cis*-7-Methylenebicyclo[4.1.0]hept-2-ene (l) | 4786.0±1.1 [91] | 208.8±1.0 | 43.2** | 252.0 | 121.2 |
| 15 | *cis*-7-Oxabicyclo[4.1.0]heptane (l) | 3624.2±1.1 [149] | −166.8±1.1 | 40.5±0.2 [149] | −126.3±1.1 | 111.3 |
| 16 | *cis*-Caran-3-ol (s) | 6178.4±3.0 [147] | −329.2±3.0 | 79.5±1.3 [83] | −249.7±3.3 | 138.9 |
| 17 | *trans*-Caran-3-ol (s) | 6164.1±2.4 [147] | −343.5±2.4 | 84.3±0.4 [83] | −259.2±2.5 | 129.4 |
| 18 | *cis*-Caran-2-ol (l) | 6200.1±1.8 [148] | −307.5±2.3 | 77.2**** | −230.3 | 147.2 |
| 19 | *cis*-Caran-4-ol (l) | 6195.5±1.2 [148] | −312.1±1.8 | 78.0±3.9 [148] | −234.1±4.3 | 143.4 |
| 20 | *cis*-Bicyclo[5.1.0]octane (l) | 5088.6±1.3 [143] | −60.3±1.3 | 43.5±0.8 [143] | −16.8±1.5 | 123.4 |
| 21a | *cis*-Bicyclo[6.1.0]nonane (l) | 5747.1±2.5 [143] | −81.1±2.5 | 49.4±0.8 [143] | −31.7±2.6 | — |
| | | 5748.4±3.7 [150] | −79.8±3.7 | 49.8±0.8 [150] | −30.0±3.8 | — |
| | | 5758.2±1.5 [86] | −70.0±1.5 | 49.4±0.8 [86] | −20.6±1.7 | 140.3 |
| 21b | *trans*-Bicyclo[6.1.0]nonane (l) | 5745.9±3.2 [150] | −82.3±3.2 | 42.7±0.6 [150] | −39.6±3.3 | — |
| | | 5760.3±1.5 [86] | −67.9±1.5 | 49.4±0.8 [86] | −18.5±1.7 | 142.4 |
| 22 | *cis*-9-Oxabicyclo[6.1.0]nonane (s) | 4936.4±2.2 [149] | −212.6±2.2 | 47.4±1.0 [149] | −165.1±2.4 | 113.8 |
| 23 | *cis*-Bicyclo[4.2.0]octane (l) | 5080.6±2.5 [143] | −68.3±2.5 | 42.7±1.2 [143] | −25.6±2.8 | 114.7 |
| 24a | *cis*-Bicyclo[3.3.0]octane (l) | 5016.0±2.8 [151] | — | — | — | — |
| | | 5012.8±1.3 [143] | −135.5±1.2 | 43.1±0.8 [143] | −92.4±1.5 | 47.8 |
| 24b | *trans*-Bicyclo[3.3.0]octane (l) | 5041.7±5.0 [151] | — | — | — | — |
| | | 5039.6±1.7 [143] | −109.0±1.6 | 42.7±0.8 [143] | −66.4±1.8 | 73.8 |
| 25a | *cis*-Bicyclo[4.3.0]nonane (l) | 5655.1±1.5 [152] | −173.1±1.5 | 46.0±1.3 [152] | −127.1±2.0 | 33.8 |
| 25b | *trans*-Bicyclo[4.3.0]nonane (l) | 5652.0±1.7 [152] | −176.2±1.7 | 44.8±1.3 [152] | −131.4±2.1 | 29.5 |
| 26 | *cis*-Bicyclo[4.3.0]nona-3,7-diene (l) | 5320.9±1.0 [153] | 64.3±1.0 | 45.0±0.9 [124] | 109.3±1.4 | 39.4 |
| 27 | *cis*-Bicyclo[5.3.0]decane (l) | 6323.7±3.3 [143] | −183.9±3.8 | 53.6±1.2 [143] | −130.3±5.0 | 51.3 |
| 28a | *cis*-Bicyclo[4.4.0]decane (l) | 6288.2±0.9 [154] | −219.4±1.1 | 50.2±2.1 [155] | −169.2±2.3 | 12.4 |
| 28b | *trans*-Bicyclo[4.4.0]decane (l) | 6277.0±0.9 [154] | −230.6±1.1 | 48.5±2.1 [155] | −182.1±2.3 | −0.5 |
| 29 | *trans*-3-Methylbicyclo[4.4.0]decane (l) | 6922.0±2.1 [11] | −264.9±2.1 | 53.5** | −211.4 | −0.4 |
| 30a | *cis*-2-Methylbicyclo[4.4.0]decane (l) | 6943.1±1.9 [156] | −243.8±2.0 | — | — | — |
| 30b | *trans*-2-Methylbicyclo[4.4.0]decane (l) | 6937.2±1.7 [156] | −249.7±1.8 | — | — | — |
| 31 | Pyrrolizidine (l) | 4564.2±3.0 [157] | −48.3±3.0 | 44.4** | −3.9 | 53.8 |
| 32 | 3,5-Dimethylpyrrolizidine (l) | 5856.8±2.0 [157] | −114.4±2.0 | 47.7±1.7 [157] | −66.7±2.5 | 63.7 |

*Obtained by L.P.Timofeeva in the Laboratory of Thermochemistry at Moscow State University.
**Calculated from the Klages formula.[103]
***The value of $\Delta H_v^\circ$ measured for bicyclo[4.1.0]hept-3-ene is quoted.
****Estimated group contributions taken from Lebedev and Miroshnichenko.[83]

The results of the measurement of the enthalpies of combustion and strain energies of condensed bicyclic hydrocarbons and their derivatives are presented in Table 8. Unsubstituted bicyclo[*n.m.*0]alkanes are also extremely interesting objects for the study of strain in cyclic compounds. The strain energies of condensed rings do not in general consist of the sum of the contributions of the constituent monocyclic moieties of the molecule, but are fairly close to this value. Two factors affecting the strain energy on formation of a bicyclic compound have been noted:[143] the change in the conformation of the rings leading to an increase of $E_S$ and the disappearance of torsional interactions causing a decrease of $E_S$. The effects of these factors approximately cancel out for many real molecules. A more rigorous approach makes it necessary to reconcile data on the enthalpies of formation, molecular geometries, and vibrational frequencies. In many cases it has been possible to calculate fairly accurately the enthalpies of formation of cyclic hydrocarbons,[114–117] but this requires a knowledge of numerous accurately measured parameters, which are in practice not always known.

In relation to unsubstituted cyclic hydrocarbons of different classes, the dependence of the strain energy on the geometrical structure of the molecules has been analysed and correlation equations have been derived.[43] It has been found that the $E_S$ in the given series of compounds is determined mainly by the change of some one structural parameter. For example, in bridged bicyclic compounds $E_S$ is determined by the change of the dihedral angle, while in condensed bicyclic compounds it is determined by the deformation of the angles at the tertiary carbon atom. This may account for the characteristic variation of $E_S$ in each series of cyclic compounds after the introduction of the same substituents.

The empirical dependence of the enthalpies of formation of bicyclo[*n*.1.0]alkanes on their structure has been examined.[46]

The influence of substitution on the strain energy of bicyclo[*n.m.*0]alkanes can be traced in relation to bicyclo-[4.1.0]heptane (norcarane), for the derivatives of which numerous experimental data have been obtained (Table 8). The substitution of a hydrogen atom at the tertiary carbon atom of the methyl group does not affect the $E_S$, in contrast

to norbornane. The introduction of an endocyclic double bond entails an appreciable decrease of $E_S$, i.e. it exerts the opposite effect compared with norbornane and cyclopropane. On the other hand, the effect of an exocyclic double bond is small.

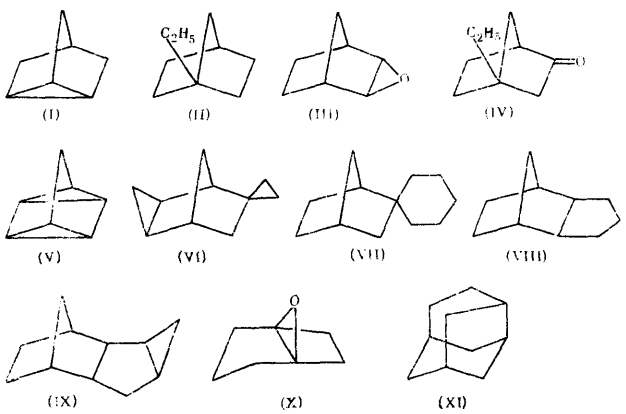
Table 8 shows that the strain energies of carane and carene (trimethyl-substituted derivatives of norcarane and norcarene) are somewhat greater than those of the initial compounds. It is of interest to note that the $E_S$ for 2-carene, whose double bond is conjugated with the three-membered ring, is greater than for 3-carene.

Many of the bicyclic compounds investigated are known only in the *cis*-form. However, in many cases $\Delta H_f^\circ$ and $E_S$ have been determined for the *cis*- and *trans*-isomers. The difference between these quantities for certain bicyclic hydrocarbons proved to be very considerable, amounting to ~10–20 kJ mol$^{-1}$ (Table 8)—see, for example, the strain energies of the *cis*- and *trans*-isomers of bicyclo[3.3.0]-octane, bicyclo[4.4.0]decane, etc.

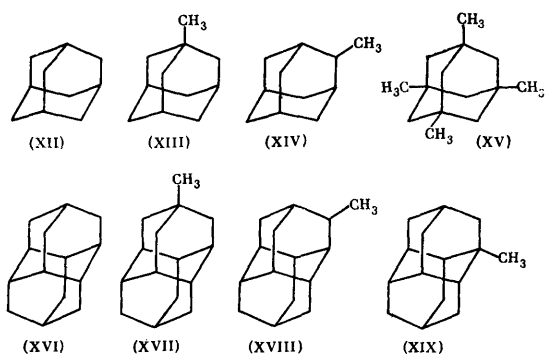
The introduction of oxygen into the three-membered ring of condensed bicyclic hydrocarbons leads to some increase in $E_S$, as in bridged bicyclic compounds. On the other hand, the presence of the OH group in the *cis*-carane structure entails an appreciable change in the strain energy regardless of its position and orientation.

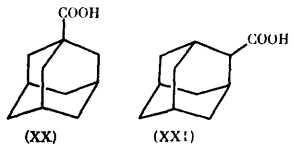
### 4. Polycyclic Hydrocarbons and Their Derivatives

Until recently, the thermochemical properties of polycyclic compounds were little investigated. However, in the last decade a number of studies, mainly of bridged polycyclic compounds (I)–(XI) containing small rings with less than six atoms in the ring have been published.

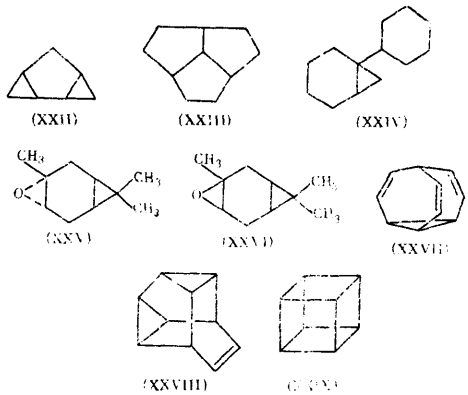



The bridged polycyclic compounds (XII)–(XXI) containing only six-membered rings (adamantane, diadamantane, and their derivatives) constitute a separate group.




A few data are available for the condensed polycyclic compounds (XXII)–(XXIX) containing different rings, including seven-membered rings.




The study of polycyclic compounds has been partly induced by practical needs, because many of them enter into the composition of petroleum and their physicochemical properties are close to those of components of lubricating oils.[165] These compounds are of even greater interest for the investigation of the influence of the structural features of molecules on the energy properties of the given substance.

Thermochemical data for polycyclic hydrocarbons and their derivatives are presented in Table 9. It has been observed for the compounds investigated that the strain energies of the majority of these molecules are smaller than the sums of the contributions of the strain energies of the individual rings constituting the molecule. In some cases the strain energy may be much higher, for example, in cubane (XXIX) and spiro{tricyclo[3.2.1.0$^{2,4}$]octane-6,1′-cyclopropane} (VI) (Table 9).

It was initially assumed that the adamantane (XII) and diadamantane (XVI) molecules are unstrained, but the experimental determination of $\Delta H_c^\circ$ showed that their strain energies are appreciable (~20–40 kJ mol$^{-1}$). This finding has been explained[115,170] by the presence of angular strain and by the interaction of non-bonded carbon atoms.

It is noteworthy that the substitution of a hydrogen atom at a tertiary carbon atom by an alkyl group in nortricyclene (VII), adamantane, and diadamantane leads to an appreciable decrease in $E_S$. The introduction of the methyl group in the 2-position, causes, on the other hand, an increase in $E_S$. These effects are similar to that of alkyl substitution on the $E_S$ for norbornane (Table 7) and can apparently be accounted for by the same causes.

## VI. THERMOCHEMISTRY OF ORGANOHALOGEN COMPOUNDS

The organohalogen compounds investigated belong to different classes. A considerable proportion of them consist of fluoro-substituted lower hydrocarbons (methane, ethylene, ethane, and propane). The $\Delta H_c^\circ$ and $\Delta H_f^\circ$ have also been determined for many chlorofluoro-derivatives as well as bromine-containing compounds.

It is noteworthy that there are still many obscure problems and even contradictions in the thermochemistry of organohalogen compounds. This can be explained mainly by the methodological difficulties noted above. In recent years determinations of $\Delta H_c^\circ$ and $\Delta H_f^\circ$ for organohalogen compounds have been made in order to establish the thermochemical properties of the compounds of greatest importance for technology, to elucidate and resolve the contradictions in the available data, and also to investigate new promising classes of organohalogen compounds (tertiary perfluoroamines, fluoro- and chlorofluoro-ethers, fluorinated diketones, etc.). For example, the measurement of the $\Delta H_c^\circ$ and $\Delta H_f^\circ$ for 1,2,2-trichloro-1,1,2-trifluoroethane, 1-bromo-2-chloro-1,1,2-trifluoroethane, and chlorotrifluoroethylene made it possible to correct (by 40–50 kJ mol$^{-1}$) the incorrect values present in the literature and to solve one of the most complex problems of the thermochemistry of organohalogen compounds.[22]

Table 9. The enthalpies of combustion, formation, and evaporation (sublimation) and the strain energies of polycyclic compounds at 298 K (in kJ mol$^{-1}$).

| Substance | $-\Delta H_c^0$ | $\Delta H_f^0$ (l or s) | $\Delta H_v^0$ or $\Delta H_s^0$ | $\Delta H_f^0$ (g) | $E_s$ |
|---|---|---|---|---|---|
| (I) (s) | 4207.8±2.1 [126] | 24.1±2.1 | 38.0±0.1 [126] | 62.1±2.1 | — |
| | 4214.8±1.0 [127] | 31.1±1.0 | 39.2±1.1 [127] | 70.3±1.5 | 164.2 |
| | 4227.1±2.0 [120] | 43.4±2.0 | 38.7±0.6 [120] | 82.1±2.1 | — |
| (I) (g) | — | — | — | 84.3±3.2 [128] | — |
| | — | — | — | 82.3 [142] | — |
| (II) (l) | 5510.0±2.1 [162] | −32.4±2.1 | 42.0±0.1 [162] | 9.6±2.1 | 156.4 |
| (III) (s, *exo*-) | 4086.9±2.6 [149] | −96.8±2.6 | 44.1±0.5 [149] | −52.7±2.7 | 180.1 |
| (IV) (l) | 5115.1±1.8 [162] | −141.5±1.8 | 49.8±0.8 [162] | −91.7±2.0 | 165.6 |
| (V) (s) | 4114.3±1.1 [126] | 216.4±1.1 | 37.0±0.1 [126] | 253.4±1.2 | — |
| | 4200.0±2.2 [120] | 302.1±2.2 | 37.0±0.8 [120] | 339.1±2.3 | 238.8 |
| (V) (g) | — | — | — | 332.7±2.9 [128] | — |
| | — | — | — | 333.0 [142] | — |
| (VI) (l, *cis*-) | 6058.5±1.6 [162] | 122.6±1.6 | 47.8±0.1 [162] | 170.4±1.6 | 303.7 |
| (VII) (l) | 7388.1±2.1 [46] | −192.3±2.1 | 57.3* | −135.0 | 65.2 |
| (VIII) (l) | 6108.8±2.5 [119] | −112.9±2.5 | 52.9±1.3 [119] | −60.0±2.8 | 96.1 |
| (IX) (l, *exo*-) | 6618.7±2.1** | 3.4±2.1 | 55.2±0.5** | 58.6±2.2 | 209.8 |
| (X) (l) | 4174.2±1.0 [163] | −9.5±1.0 | 36.4 [163] | 26.9 | 281.9 |
| (XI) (s) | 6070.9±1.7 [159] | −150.8±1.7 | 64.8±1.8 [159] | −86.0±2.5 | 62.1 |
| (XII) (s) | 6024.5±0.7 [167] | −197.2±0.7 | 59.3±0.2 [167] | −137.9±0.7 | 18.2 |
| | 6033.1±2.8 [119] | −188.6±2.8 | 60.5±1.3 [119] | −128.1±3.1 | 28.0 |
| | 6033.4±3.3 [168] | −188.3±3.3 | 59.5±0.8 [168] | −128.8±3.4 | 27.3 |
| | 6029.2±0.4 [159] | −192.5±0.4 | 59.7±0.8 [159] | −132.8±0.9 | 23.3 |
| (XIII) (s) | 6663.8±1.3 [159] | −237.3±1.3 | 67.6±0.5 [159] | −169.7±1.4 | 18.5 |
| (XIV) (s) | 6684.4±1.2 [159] | −216.7±1.2 | 67.5±2.1 [159] | −149.2±2.4 | 39.0 |
| (XV) (s) | 8577.0±2.0 [159] | −362.1±2.0 | 81.1±0.9 [159] | −281.0±2.2 | 3.6 |
| (XVI) (s) | 8127.7±1.3 [159] | −239.7±1.3 | 95.9±0.8 [159] | −143.8±1.5 | 44.1 |
| | 8084.8±1.7 [169] | −282.6±1.7 | 87.0±1.9 [169] | −195.6±2.5 | — |
| (XVII) (s) | 8785.2±0.7 [159] | −261.5±0.7 | 79.4±1.2 [159] | −182.1±2.0 | 37.9 |
| (XVIII) (s) | 8786.4±2.0 [159] | −260.4±2.0 | 103.1±1.0 [159] | −157.3±2.3 | 60.0 |
| (XIX) (s) | 8799.4±3.3 [159] | −247.4±3.3 | 80.6±0.4 [159] | −166.8±3.3 | 53.2 |
| (XX) (s) | 5972.2±3.6 [170] | −643.1±3.6 | — | — | — |
| (XXI) (s) | 5988.1±3.8 [170] | −627.2±3.8 | — | — | — |
| (XXII) (l, *trans*-) | 4296.5±1.3 [158] | 112.8±1.3 | 36.5±0.5 [139] | 149.3±1.4 | 243.2 |
| (XXIII) (s) | 6662.8±3.2 [159] | −158.9±3.2 | 56.6±1.3 [159] | −102.3±3.6 | 53.8 |
| (XXIV) (l) | 8094.1±2.9 [160] | −165.7±2.9 | 57.2* | −108.5 | 112.4 |
| (XXV) (l, α-) | 6065.4±1.5 [161] | −156.3±1.5 | 49.4* | −106.9 | 228.0 |
| (XXVI) (l, β-) | 6073.7±1.6 [161] | −148.0±1.6 | 50.2* | −97.8 | 237.1 |
| (XXVII) (s) | 5626.5±3.0 [164] | 262.3±3.0 | 71.8±0.4 [164] | 334.1±3.0 | 146.1 [164] |
| (XXVIII) (s) | 5610.7±2.1 [165] | 246.4±2.1 | — | — | — |
| (XXIX) (s) | 4833.2±3.3 [166] | 541.8±3.3 | 80.3±1.7 | 622.1±3.7 | 685.6 |

*Calculated from the Klages formula.[103]
**The measurements were carried out by L.P.Timofeeva and L.L.Pashchenko in the Laboratory of Thermochemistry at Moscow State University.

The publication of numerous new experimental data made it necessary to revise the entire set of enthalpies of formation of organohalogen compounds. This revision is particularly urgently required also because until recently there has been a considerable lack of coordination in the selection of key quantities for the calculation of $\Delta H_f^\circ$. This virtually precluded the analysis of the experimental data and the search for thermochemical relations on the basis of the results of different workers.

In order to represent and analyse the entire experimental thermochemical data for organohalogen compounds on a modern basis, the $\Delta H_f^\circ$, both those obtained in the Laboratory of Thermochemistry at Moscow State University and the available literature data, were recalculated by ourselves on the basis of a single system of key quantities developed and adopted by CODATA.[32] Analysis of the available experimental data for different groups of organohalogen compounds led Kolesov[171] to the following results. In the case of halogenomethanes, the most reliable $\Delta H_f^\circ$ for 17 compounds were selected and on their basis the $\Delta H_f^\circ$ for all the remaining halogenomethanes were calculated by approximate estimation methods.[171] Among the halogenoethanes, reliable $\Delta H_f^\circ$ were selected for 37 compounds and the $\Delta H_f^\circ$ for all the possible 210 bromochlorofluoroethanes were calculated on the basis of these reference quantities in terms of the approximation of atom–atom pair interactions.[172]

A somewhat greater number of reliable $\Delta H_f^\circ$ values are available in the literature for the halogeno-derivatives of saturated aliphatic compounds. The enthalpies of formation of saturated fluoro- and chlorofluoro-derivatives of organic compounds ($n \geq 3$, where $n$ is the number of carbon atoms) are presented in Table 10, which embraces all the data known at present except the $\Delta H_f^\circ$ for methane and ethane derivatives as well as Swarts's obsolete data.[199] To facilitate the calculation of certain constants entering into computational schemes and to revise their values, Table 10 also includes two compounds without fluorine, namely propyl chloride and 1,1,1,3-tetrachloropropane. The majority of the quantities listed in Table 10 have been obtained experimentally in the Laboratory of Thermochemistry at Moscow State University. The experimental data have been analysed and the choice of the $\Delta H_f^\circ$ for compounds Nos.1–9 and 16–19 has been justified by Kolesov.[200] The numerical differences between the $\Delta H_f^\circ$ for the compounds in Table 10 and those quoted by Kolesov[200] can be due only to the recalculation in terms of the SI system of units and the recalculation in terms of the system of key quantities adopted by CODATA (see above). The details of the experimental determination of all the values of $\Delta H_f^\circ$ are given in the corresponding communications quoted in Table 10. The $\Delta H_v^\circ$ obtained from calorimetric and ebulliometric measurements were used to calculate the $\Delta H_f^\circ$(gas).[201–204] In those cases where the experimental data were lacking, the enthalpies of evaporation were estimated from the Klages[103] and Kistiakowsky[205] equations.

The experimental data were treated by Tatevskii's method.[70,206,207] Preliminary analysis showed[208,209] that at least a scheme taking into account the atoms in the first and second interaction spheres should be adopted as a single computational scheme which would ensure an accuracy of the calculation comparable to the experimental accuracy. However, the experimental data available at present are clearly insufficient for the calculation of all the constants involved in such a scheme. The experimental enthalpies of formation of the organofluorine compounds were therefore treated as follows.[208]

In the first place the constants necessary for the evaluation of the $\Delta H_f^\circ$ in accordance with the scheme involving "atoms in the first interaction sphere" were calculated from the available experimental data. In setting up this computational scheme, we began with the usual classification of structural elements, i.e. we took into account the chemical nature and valence state of the given atom and also the

chemical nature and valence state of the atoms linked directly to the given atom.[72] The structural elements were designated by the system of symbols taken from Benson et al.[40], which is fully consistent with the characteristics of the structural elements in the scheme involving atoms where the first interaction sphere is taken into account. In order to limit reasonably the number of unknowns, the contributions of the structural elements not containing halogens were taken from the same investigation.[40]

The enthalpies $\Delta H_f^\circ$ for 41 compounds (Table 10) were treated by the method of least squares. Comparison of the calculated and experimental $\Delta H_f^\circ$ shows that the computational scheme employed is extremely approximate and that the difference between the calculated and experimental values $\Delta(\Delta H_f^\circ)$ is several times greater than the experimental error in some cases. This comparison makes it possible to discover also groups of compounds for which the deviations $\Delta(\Delta H_f^\circ)$ are a maximum. This applies in the first place to perfluoroalkanes and substances where the perfluoro-group ($CF_3$ or $-CF_2-$) adjoins the $-CH_2-$ group. Appreciable discrepancies have also been observed for certain ethers. For the remaining compounds, the scheme involving atoms and their first environment as a rule yields satisfactory results.

In order to reduce the most serious of the discrepancies noted above, the calculation of $\Delta H_f^\circ$ in accordance with the "atoms in the first interaction sphere" scheme was refined by partial allowance for the second interaction sphere. Since the limited amount of experimental data precluded the complete allowance for the second interaction sphere, account was taken only of the second interaction sphere of the oxygen atom in the ethyl group and the carbon atom in the perfluoro-groups. For this purpose, the structural elements incorporating the second interaction sphere of the oxygen atom in ethers were identified, i.e. $O-(CF_2)(CF_2)$, $O-(CF_2)(CH_2)$, $O-(CF_2)(CCl_2)$, $O-(CF_2)(CCl_3)$, $O-(CF_2)(CH_3)$, and $O-(CF_2)(CF_2Cl)$. The perfluoro-groups were subdivided into two categories: the $C-(F)_3[C_F]$ and $C-(F)_2.[C_F]_2$ groups, adjoining only fluorine-containing groups even though these may not be fully fluorinated ($CF_2H$, $CF_3$, CFH, $CF_2$, CFCl, etc.) and the $C-(F)_3(CH_2)$ and $C-(F)_2(C).(CH_2)$ groups linked to at least one $-CH_2-$ group. Unfortunately a more detailed differentiation of the perfluoro-groups is so far impossible owing to the insufficiency of experimental data.

**Table 10.** Comparison of the experimental and calculated $\Delta H_f^\circ(g)$ for organohalogen compounds (in kJ mol$^{-1}$).

| No. | Substance | $-[\Delta H_f^0(g)]_{exp}$ | $-[\Delta H_f^0(g)]_{c,I}$ | $\Delta[\Delta H_f^0(g)]_I$ | $-[\Delta H_f^0(g)]_{c,II}$ | $\Delta[\Delta H_f^0(g)]_{II}$ |
|---|---|---|---|---|---|---|
| 1 | $CF_3-CF_2-CF_3$ | 1784.7±8.8 [173] | 1789.1 | +4.4 | 1762.9 | −21.8 |
| 2 | $CF_3-(CF_2)_5-CF_3$ | 3385.4±7.1 [174] | 3437.2 | +51.8 | 3402.5 | +17.1 |
| 3 | $1/n[-CF_2-CF_2-]_n$ | 809.6 [175.176] | 824.1 | +14.5 | 819.5 | +10.2 |
| 4 | $CH_3-CFH-CH_3$ | 286.2±3.0 [177] | 301.9 | +15.7 | 286.2 | 0 |
| 5 | $CH_3-CH_2-CH_2F$ | 279.4±2.6 [177] | 279.1 | 0 | 279.4 | 0 |
| 6 | $CF_3-CH_2-CF_3$ | 1406.1±8.1 [178] | 1397.7 | −8.4 | 1413.5 | +7.2 |
| 7 | $1/n[-CF_2-CH_2-]_n$ | 465.9 [180] | 432.7 | −33.2 | 462.8 | −3.1 |
| 8 | $CF_3-CH_2-CH_2Cl$ | 779.7±2.2 [181] | 774.5 | −5.2 | 780.6 | +0.9 |
| 9 | $CF_3-CH_2-CCl_3$ | 803.9±2.2 [181] | 794.4 | −9.5 | 799.2 | −4.7 |
| 10 | $CF_3-CH_2-CHCl_2$ | 791.3±2.7 [182] | 791.3 | 0 | 791.3 | 0 |
| 11 | $CH_3-CH_2-CH_2Cl$ | 132.5±1.0 [183] | 128.2 | −4.3 | 126.6 | −5.9 |
| 12 | $CCl_3-CH_2-CH_2Cl$ | 161.7±1.7 [184] | 171.2 | +9.5 | 166.3 | +4.6 |
| 13 | $CF_3-CFCl-CF_2Cl$ | 1324.7 [185.186] | 1325.0 | +0.3 | 1320.4 | −4.3 |
| 14 | $CF_3-CH_2-CFCl_2$ | 970.3 [182] | 970.0 | −0.3 | 972.9 | +2.6 |
| 15 | $CF_3-CH_2-CF_2Cl$ | 1151.5±3.6 [182] | 1151.2 | −0.3 | 1153.8 | +2.3 |
| 16 | $CF_3-CH_2-CH_2-OH$ | 921.0±2.5 [187] | 903.3 | −17.7 | 911.1 | −9.9 |
| 17 | $CF_2H-CF_2-CH_2-OH$ | 1064.8±2.7 [187] | 1067.6 | +2.8 | 1064.8 | 0 |
| 18 | $CF_3-CF_2-CH_2-OH$ | 1309.1±4.3 [187] | 1294.6 | −14.5 | 1312.8 | +3.7 |
| 19 | $CF_3-CF_2-CF_2-CH_2-OH$ | 1739.7±7.9 [179.188] | 1706.7 | −33.0 | 1722.7 | −17.0 |
| 20 | $(CF_3-CH_2-CH_2)_2O$ | 1604.4±4.0 [189] | 1586.1 | −18.3 | 1601.7 | −2.7 |
| 21 | $(CF_3-CF_2-CF_2)_2O$ | 3148.2±9.5 [190] | 3156.5 | +8.3 | 3158.0 | +9.8 |
| 22 | $(CF_3-CF_2-CF_2-CF_2)_2O$ | 3979.2±12.0 [182] | 3980.5 | +1.3 | 3977.8 | −1.4 |
| 23 | $(CF_3-CF_2-CF_2-CF_2-CF_2)_2O$ | 4806.4±20.7 [191] | 4804.6 | −1.8 | 4797.6 | −8.8 |
| 24 | $CFCl_2-CF_2-O-CCl_3$ | 901.2±2.9 [192] | 901.5 | +0.3 | 898.7 | −2.5 |
| 25 | $CF_3-CFCl-CF_2-O-CCl_3$ | 1524.1±4.9 [192] | 1523.8 | −0.3 | 1526.4 | +2.3 |
| 26 | $CFClH-CF_2-O-CH_3$ | 882.3±2.1 [192] | 869.4 | −12.9 | 882.3 | 0 |
| 27 | $CFClH-CF_2-O-CH_2-CF_2-CF_2H$ | 1720.7±5.0 [193] | 1736.3 | +15.6 | 1736.4 | +15.7 |
| 28 | $CFClH-CF_2-O-CH_2-(CF_2)_3-CF_2H$ | 2555.6±7.3 [193] | 2560.4 | +4.8 | 2556.2 | +0.4 |
| 29 | $CFClH-CF_2-O-CH_2-(CF_2)_5-CF_2H$ | 3391.9±11.0 [193] | 3384.4 | −7.5 | 3376.0 | −15.9 |
| 30 | $CF_3-CFH-CF_2-O-CH_2-CF_2-CF_2H$ | 2359.5±8.0 [194] | 2341.1 | −18.4 | 2351.5 | −8.0 |
| 31 | $CF_3-CFH-CF_2-O-CH_2-(CF_2)_3-CF_2H$ | 3162.4±12.4 [194] | 3165.1 | +2.7 | 3171.3 | +8.9 |
| 32 | $CFCl_2-CF_2-O-CF_2Cl$ | 1325.6±7.3 [195] | 1325.6 | 0 | 1325.6 | 0 |
| 33 | $CFCl_2-CF_2-O-CCl_2-CF_2-CF_2Cl$ | 1752.5±6.5 [195] | 1744.5 | −8.0 | 1746.5 | −6.0 |
| 34 | $CFCl_2-CF_2-O-CCl_2-(CF_2)_3-CF_2Cl$ | 2560.6±8.3 [195] | 2568.6 | +8.0 | 2566.3 | +5.7 |
| 35 | $(CF_2)_4(CH_2OH)_2$ | 2084.2±12.0 [196] | 2036.3 | −47.8 | 2092.4 | +8.2 |
| 36 | $CF_3-CF_2-COOCH_3$ | 1428.3±3.7 [189] | 1440.4 | +12.1 | 1433.5 | +5.2 |
| 37 | $CF_3-CF_2-CF_2-COOCH_3$ | 1843.0±7.3 [197] | 1852.4 | +9.4 | 1843.4 | +0.4 |
| 38 | $(CF_2)_3(COOCH_3)_2$ | 1926.6±5.7 [191] | 1915.8 | −10.8 | 1923.9 | −2.7 |
| 39 | $CF_3-N(CF_2-CF_3)_2$ | 2783.2±9.1 [27] | 2783.2 | 0 | 2783.2 | 0 |
| 40 | $(CF_3-CF_2)_3N$ | 3172.4±12.3 [198] | 3172.1 | −0.3 | 3177.2 | +4.8 |
| 41 | $(CF_3-CF_2-CF_2-CF_2)_3N$ | 5643.9±19.8 [198] | 5644.3 | +0.4 | 5636.6 | −7.3 |

Notation. $[\Delta H_f^\circ(g)]_{exp}$ is the experimental standard enthalpy of formation of the gaseous compound, while $[\Delta H_f^\circ(g)]_{c,I}$ and $[\Delta H_f^\circ(g)]_{c,II}$ are the values calculated respectively taking into account the first environment and with partial allowance also for the second environment.

**Table 11.** The contribution of atoms to $\Delta H_f^\circ(g)$ taking into account their first and in some cases also the second interaction sphere (in kJ mol$^{-1}$).

| Atoms and their environment | Contribution to $\Delta H_f^0(g)$ | Atoms and their environment | Contribution to $\Delta H_f^0(g)$ |
|---|---|---|---|
| $C-(F)_3[C_F]$ | −676.5 | $C-(Cl)(H)_2(C)$ | −63.6 |
| $C-(F)_3(CH_2)$ | −696.3 | $O-(CF_3)(CCl_3)$ | −642.8 |
| $C-(F)_2(Cl)(C)$ | −436.8 | $O-(CF_2)(CH_3)$ | −619.1 |
| $C-(F)(Cl)_2(C)$ | −255.9 | $O-(CF_2)(CF_2Cl)$ | −1069.8 |
| $C-(F)_2(H)(C)$ | −428.2 | $O-(CF_2)(CF_2)$ | −985.2 |
| $C-(F)(Cl)(H)(C)$ | −263.2 | $O-(CF_3)(CCl_3)$ | −643.9 |
| $C-(F)(H)_2(C)$ | −216.1 | $O-(CF_2)(CH_2)$ | −602.8 |
| $C-(F)_2[C_F]_2$ | −409.9 | $C-(H)_3(C)$ | −42.2 |
| $C-(F)_2(C)(CH_2)$ | −442.2 | $C-(H)_2(C)_2$ | −20.7 |
| $C-(F)(Cl)(C)_2$ | −207.1 | $C-(O)(C)(H)_2$ | −35.6 |
| $C-(F)(H)(C)_2$ | −201.8 | $O-(H)(C)$ | −158.5 |
| $C-(F)_2(CO)(C)$ | −402.3 | $O-(C)_2$ | −96.5 |
| $C-(F)_3(N)$ | −699.1 | $C-(H)_3(O)$ | −42.2 |
| $C-(F)_2(N)(C)$ | −416.6 | $O-(CO)(C)$ | −172.8 |
| $C-(Cl)_3(C)$ | −82.1 | $CO-(O)(C)$ | −139.7 |
| $C-(Cl)_2(H)(C)$ | −74.3 | $N-(C)_3$ | +102.1 |

Partial allowance for the second environment led to an increase of the constants of the additive scheme from 19 to 23. They were evaluated by the method of least squares in accordance with a standard program. The constants of these, i.e. the energy contributions to the $\Delta H_f^\circ$ from structural elements, are presented in Table 11, which includes also nine contributions taken from Benson et al.[40]. The $\Delta H_f^\circ$ calculated from the contributions in Table 11 are given in the sixth column of Table 10. It is seen from Table 10 that the differences between the calculated and experimental $\Delta H_f^\circ$ as a rule do not exceed the experimental error. Only for a few compounds does the discrepancy $\Delta(\Delta H_f^\circ)$ exceed 10 kJ mol$^{-1}$. These discrepancies can probably be accounted for by the incomplete allowance for the second environment of the atom. On the other hand, overall comparison of the experimental and calculated $\Delta H_f^\circ$ shows that the additive computational scheme, taking into account fully the first environment and partly the second environment of the atoms, is fully applicable in the approximate calculation of the standard enthalpies of formation of fluoro- and chlorofluoro-derivatives of organic compounds.

## VII. CONCLUSION

Thus it follows from the present review that the capacity of lactams, their *N*-methyl derivatives, and cyclic formals for polymerisation can be fairly fully characterised by thermodynamic functions obtained using calorimetric methods. The problem whether or not polymerisation reactions of other cyclic compounds are thermodynamically allowed still remains acute. For this reason, studies of the thermodynamics of the polymerisation reactions of cyclic compounds of different classes are being continued and will apparently continue to develop in the immediate future.[211,212] Studies carried out in recent years made it possible to generalise and refine the earlier conclusions. It has been established that the polymerisation of three-, four-, five-, seven-, eight-, and many six-membered rings of different chemical nature is thermodynamically allowed. On the other hand, the polymerisation reactions of acyclic monomers, leading to the formation of highly structured thermally stable polymers with cyclic fragments, have aroused much interest in recent years. The thermodynamics of reactions of this type, for example, the cyclotrimerisation of aryl cyanates, isocyanates, etc. has been vigorously investigated[213] and these studies will undoubtedly continue to develop.

Despite the fairly extensive experimental data, few reliably established relations are so far available in the thermochemistry of cyclic hydrocarbons and their derivatives. Some of them were noted above in the analysis of the $\Delta H_f^\circ$ for compounds with small rings and also with rings separated by a single bond. For compounds with a more complex structure (bicyclic bridged compounds, condensed bicyclic compounds, etc.), the experimental data obtained show that, as a rule, a characteristic dependence of the $\Delta H_C^\circ$ and $E_S$ on the nature, positions, and numbers of substituents in the molecule has been observed for each series of compounds. Extrapolation of the relations found for any one series of cyclic compound to other groups of compounds can lead to large errors. The study of the energetic and structural characteristics of cyclic compounds is therefore inevitably associated with the need for a fairly large set of reliable experimental data, particularly for methyl- and ethyl-substituted derivatives. They should be regarded as the first series members having unusual properties, which is analogous to the consideration of methane or ethane in the series of n-alkanes.

The numerical values of the strain energy have been used in the present review mainly for the analysis of thermochemical relations for particular groups of compounds. However, they can be useful also for the parametrisation of various empirical force field methods in order to calculate the $\Delta H_f^\circ$(gas) for cyclic compounds.[114-117]

The set of investigations carried out in the thermochemistry of organohalogen compounds has already made it possible to set up a system of thermochemical data by means of which it is possible to calculate approximately the enthalpies of formation of numerous compounds which have not yet been investigated. The accuracy of the calculations for the fluoro- and chlorofluoro-substituted n-alkanes is comparable to the accuracy of the determination of the experimental quantities.[172,208]

The further development of the thermochemistry of organohalogen compounds will apparently be determined by the investigation of new promising classes of substances and the accumulation of reliable experimental data for "reference" compounds.

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# The Luminescence-spectroscopic Properties of Aromatic Radicals and Biradicals

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The luminescence-spectroscopic characteristics (the parameters of the absorption and luminescence spectra and the lifetimes and conditions in the observation of luminescence) of the radical products of the photolysis of aromatic compounds, namely abstraction radicals, hydro-radicals, radical-ions, and biradicals, are examined.
The bibliography includes 158 references.

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## I. INTRODUCTION

The study of the luminescence-spectroscopic properties of polyatomic molecular systems can yield information about the nature and characteristics of the processes involved in the evolution of electronically excited molecular states. A number of problems of practical importance have made such research particularly timely. Among these we may mention the problem of the selection and creation of active media for lasers based on solutions of organic compounds, the development of methods of synthesis of effective organic phosphors and scintillators, the development of systems for the photochemical recording of information, the creation of photostable and radiation-chemically stable systems, etc.

The luminescence-spectroscopic properties of organic molecules have been so far studied in adequate detail and at sufficient depth and the general characteristics of their dependence on the electronic structure of the molecules have been established.[1-5] The principal stages in the development of such investigations are associated with the development of orbital models to describe the electronically excited molecular states, the study of the fine structure of vibronic states, and the development of theoretical ideas about the nature and characteristics of non-radiative conversion processes.

The problem of the determination of a relation between luminescence-spectroscopic properties and the structure of radicals and biradicals derived from organic compounds, which are the primary products of the photochemical and radiation-chemical reactions, has been solved to a much lesser extent. It is essential that they be solved because luminescence (together with EPR) is one of the main procedures whereby the decomposition products of the initial compounds can be detected. Furthermore, a luminescence analysis makes it possible to determine the electronic state in which the decomposition product is formed and hence to understand the mechanism of the process.

We may mention further that at advanced stages of photolytic (or radiolytic) processes, the radicals and biradicals themselves react and the mechanisms of such reactions cannot be understood without the knowledge of the nature of their electronic states.

The present review gives a systematic account of experimental luminescence-spectroscopic data for the radicals, biradicals, and radical-ions derived from aromatic compounds together with their interpretation based on molecular orbital ideas concerning the nature of the electronically excited states and the general characteristics of the processes involved in radiative and non-radiative evolution. Since these ideas and characteristic features have been described in a number of reviews in recent years,[2,4,5] in the present review we will confine ourselves to a brief description.

## II. GENERAL CHARACTERISTICS OF THE LUMINESCENCE OF POLYATOMIC MOLECULAR SYSTEMS

The electronic states of radicals and biradicals, like those of molecules, can be classified in terms of the multiplicity of the given states. The electronic states of molecules and biradicals can be of the singlet ($S$) and triplet ($T$) types, because these systems contain an even number of electrons. In the majority of molecules, the ground state is of the singlet type ($S_0$) and the electronically excited state with the lowest energy is of the triplet type. The ground state of the majority of known biradicals is of the triplet type. In conformity with the fact that radicals contain an odd number of electrons, they can have either doublet ($D$) or quartet ($Q$) electronic states. The ground state of known radicals derived from organic compounds is of the doublet type ($D_0$). The lowest electronically excited state in most cases is a $D$ state, while $Q$ states have a higher energy.

Another important characteristic feature of excited states is their orbital nature. Ideas concerning the orbital nature of the electronic transitions and electronically excited states, which have been developed in detail for planar $\pi$-electron systems, can be used without any changes for planar radicals and biradicals. Accordingly, $S_{\pi\pi^*}$, $S_{n\pi^*}$, $T_{\pi\pi^*}$, $T_{n\pi^*}$, etc. states are possible in biradicals, whereas $D_{\pi\pi^*}$, $D_{n\pi^*}$, $Q_{\pi\pi^*}$, $Q_{n\pi^*}$ states are possible in radicals. For systems

with a non-planar structure, states of the $n\pi^*$ and $\pi\pi^*$ types cannot, strictly speaking, be separated even in terms of the Condon approximation. However, when the deviations of the geometrical structure of the system from planarity are small or when the $\pi$ and $n$ orbitals are separated by large energy gaps, the lowest excited states of the system can be approximately classified as $\pi\pi^*$, $n\pi^*$, etc. states.[6] As for molecules, we shall retain designations of the type $S_0$, $T_0$, and $D_0$ for the ground state, because they are adequate for the description of the luminescence-spectroscopic properties (we may note that they can be specified in greater detail for the purpose of the EPR method). Here we shall also not dwell on the differentiation of the $\pi\pi^*$ and $n\pi^*$ states of molecular systems containing $l$ and $\nu$ orbitals.[4]

Two principal channels leading to the decomposition of electronically excited states of photostable polyatomic systems are known to exist, namely the photon emission process (luminescence) and non-radiative conversion processes in which the energy of the electronic excitation is converted into the vibrational energy of the nuclei of the system. The probability of both is governed significantly by the orbital nature and multiplicity of the combining states and (especially for the conversion processes) by the transition energy. The general features which determine the probability of the radiative processes and the non-radiative conversion processes as a function of the structure of the molecular system have been to a large extent elucidated for $\pi$-electron molecules. Some of them can be transferred to polyatomic radicals and biradicals without significant changes, while others must be somewhat modified taking into account the characteristic features of the structures of these systems and the form of their energy spectra. Here we shall discuss briefly these features emphasising their similarity and differences in the case of molecules, radicals, and biradicals.

### (a) Radiative Transitions

The probability of radiative transitions between states of identical multiplicity (fluorescence in the case of emission) is determined by the orbital nature of the transition. Since the expressions for the probability of a radiative transition in molecules, radicals, and biradicals, contain isotypical matrix elements of the dipole moment of the transition, the features found for molecular systems can be used also for radicals and biradicals. In the case of the symmetry-allowed $\pi \rightarrow \pi^*$ transitions ($D_0 \rightarrow D_{\pi\pi^*}$, $T_0 \rightarrow T_{\pi\pi^*}$, $S_0 \rightarrow S_{\pi\pi^*}$) the dipole moment of the transition $e\langle\pi|\mathbf{r}|\pi^*\rangle$ (where $\mathbf{r}$ is the radius-vector of the electron and $e$ its charge) is approximately 1 a.u., the oscillator strength $f \cong 0.1-1$ and the radiative lifetime $\tau_r$ of the excited state is $\sim 10^{-8} - 10^{-9}$ s. If the $\pi \rightarrow \pi^*$ transition is symmetry-prohibited, its probability may be found to be non-zero only on going outside the framework of the Condon approximation. The oscillator strength is then reduced to approximately $10^{-3} - 10^{-4}$ and $\tau_r$ is increased to $\sim 10^{-6}$ s.[7]

The $n \rightarrow \pi^*$ electronic transition is allowed in terms of the Condon approximation only when the $n$ orbital contains an admixture of an atomic $s$ orbital. The oscillator strength of such a transition is approximately $10^{-3}$ and $\tau_r \cong 10^{-6}$ s.[8] For the symmetry-prohibited $n \rightarrow \pi^*$ transitions, the oscillator strength is $\sim 10^{-4} - 10^{-5}$ and the lifetime is $\sim 10^{-5}$ s.[9] We may note that, when the steric structure of the system deviates from planarity, the $n\pi^*$ and $\pi\pi^*$ states of the corresponding planar configuration are mixed and the probability of a transition genealogically related to the $n \rightarrow \pi^*$ transition increases.

The probability of multiplicity-prohibited transitions depends on the energy of the spin-orbital coupling of states of different multiplicity, which depends in its turn on the orbital nature of the interacting states. The matrix elements for the spin-orbital coupling of states (of identical orbital nature) of planar molecular systems are small, because they contain only the three-centre one-electron integrals and two-electron integrals. They are estimated as approximately 0.1 $cm^{-1}$.[10,11] The matrix elements of the spin–orbital coupling of electronic states of different orbital nature (for example, $n\pi^*$ and $\pi\pi^*$) include one-centre one-electron integrals, which are proportional to $Z^4$, where $Z$ is the effective charge of the atomic nucleus carrying the $n$ electrons. For this reason, the matrix elements $|\langle S_{\pi\pi^*}|\hat{H}_{SO}|T_{n\pi^*}\rangle|$ and $|\langle S_{n\pi^*}|\hat{H}_{SO}|T_{\pi\pi^*}\rangle|$ are relatively large, amounting to approximately 100 $cm^{-1}$.[12] The matrix elements $|\langle D_{n\pi^*}|\hat{H}_{SO}|Q_{\pi\pi^*}\rangle|$ and $|\langle D_{\pi\pi^*}|\hat{H}_{SO}|Q_{n\pi^*}\rangle|$ can reach values of the same order of magnitude. Such a large difference between the coupling energies of states of the same and different orbital nature and the difference between the probabilities of the multiplicity-allowed $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions lead to significant differences between the probabilities of the multiplicity-prohibited $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

Since the $T_{n\pi^*}(Q_{n\pi^*})$ states are linked by a comparatively strong spin–orbital coupling with the $S_{\pi\pi^*}(D_{\pi\pi^*})$ states and the probability of the $S_0 \rightarrow S_{\pi\pi^*}$ ($D_0 \rightarrow D_{\pi\pi^*}$) transitions is high, the radiative lifetime of the $T_{n\pi^*}(Q_{n\pi^*})$ states is comparatively short. For molecular systems, it amounts to approximately $10^{-4} - 10^{-3}$ s.[1-4] For reasons which are clear from the foregoing, the radiative lifetime corresponding to the $T_{\pi\pi^*} \rightarrow S_0$ and $Q_{\pi\pi^*} \rightarrow D_0$ transitions is, unlike the previous case, large, amounting to 0.1–10 s.[1-4]

### (b) Non-radiative Conversion Processes

Such processes are understood as processes involving the conversion (total or partial) of the electronic excitation energy of the system into vibrational energy. Two types of conversion processes are distinguished in molecular systems: the internal conversion processes ($S-S$ and $T-T$) and intersystem crossing processes: singlet–triplet ($S-T$) and triplet–singlet ($T-S_0$) (degradation processes). The internal conversion processes take place as a consequence of non-adiabatic interaction, while intersystem crossing processes are possible only with participation of spin–orbital coupling.

The probability of internal conversion processes diminishes exponentially with increase of the transition energy.[13] If the transition energy exceeds approximately 2.5 eV, the probability of this process is less than the probability of emission and intersystem crossing. In this case the contribution of the internal conversion process may be neglected in the description of the evolution of the electronically excited state. Such a situation is observed in reality for many polyatomic aromatic molecules in the transition between the lowest excited $S_1$ state and the ground $S_0$ state.[14] In molecules containing a comparatively small number of atoms (for example, in benzene and its simplest derivatives) the $\pi \rightarrow \pi^*$ electronic excitation entails an appreciable decrease of the lengths of the C–H bonds whose stretching vibrations play the role of promoting vibrations in the internal conversion process. This leads to such a significant increase of the probability of the internal conversion that it becomes close to the probability of emission and $S-T$ conversion even for transitions with energies exceeding approximately 2.5 eV.[13]

If the transition energy is 1.5–2.5 eV, then the probability of internal conversion for polyatomic molecules and molecules with a comparatively small number of atoms is similar to, as regards order of magnitude, or exceeds the probability of emission and $S-T$ conversion. In this case the internal conversion process competes with other processes leading to the decomposition of the excited state and the role of conversion increases with decrease of the transition energy.

Finally, if the transition energy is less than approximately 1 eV, the main pathway to the decomposition of the excited state becomes the internal conversion process whose rate constant exceeds $10^{11}$ $s^{-1}$ and it suppresses the emission process. This energy range is characteristic of transitions between the electronically excited states of molecular systems: the very low (approximately $10^{-4}$) quantum yields of the fluorescence in the highest excited states are due to this factor (Kasha's rule[1]). The internal conversion process is characterised by an isotope effect (H/D) whose magnitude increases sharply (exponentially) with the increase of the transition energy. If the conversion process competes with the emission process, then the isotope effect affects also the fluorescence yield.[15]

Thus, since, as shown below, the energy of the long-wavelength multiplicity-allowed transition is much smaller for radicals and biradicals than for molecules, the internal conversion process ($D_1-D_0$ or $T_1-T_0$) in radicals may compete with the fluorescence process and the fluorescence quantum yield should be sensitive to isotopic H/D substitution; such a situation has indeed been observed experimentally. As for molecules, the yield of the fluorescence from the highest excited states of radicals and biradicals cannot be high.

The probability of the intersystem crossing (degradation) processes depends on the energy of the spin–orbital coupling of the combining states and diminishes exponentially with increase of the transition energy. Since the energy of the spin–orbital coupling of states of different orbital nature is relatively high (see above), the probability of the conversion processes $S_{\pi\pi^*} \rightsquigarrow T_{n\pi^*}$ and $S_{n\pi^*} \rightsquigarrow T_{\pi\pi^*}$ is also high and the rate constant is approximately $10^{10}-10^{11}$ $s^{-1}$ for molecules.[2,4] If there is a possibility of processes of this type, the fluorescence quantum yield is very low, (approximately $10^{-3}-10^{-4}$). In conformity with the fact that the spin–orbital coupling of states of an identical orbital nature is weak, the probability of the $S_{\pi\pi^*} \rightsquigarrow T_{\pi\pi^*}$ and $S_{n\pi^*} \rightsquigarrow T_{n\pi^*}$ conversion processes is appreciably lower and amounts to approximately $10^7-10^9$ $s^{-1}$.[2,4] Consequently processes of this kind can compete with the fluorescence process but do not lead to the complete suppression of the latter. The relations between the processes involved in the evolution of excited states described above serve as a basis for a systematic treatment of molecules in terms of their luminescence-spectroscopic properties.[16,17] These features can be transferred without any changes to the $S \rightarrow T$ and $T \rightarrow S$ transitions in biradicals and the $D \rightarrow Q$ transitions in radicals. In particular, it is shown below that, when there is a possibility of intersystem crossing between the excited states of different orbital nature, the fluorescence yield of biradicals is very low.

In the case of intersystem non-radiative transitions to the ground state where the probability of the transition depends on the spin–orbital coupling, the dependence of such probability on the transition energy, which has been studied in detail both experimentally and theoretically for molecular systems,[2,4,18,19] becomes of primary importance. A sharp decrease of the phosphorescence yield with decrease of the energy of the $T \rightarrow S_0$ transition is a consequence of this dependence. Such behaviour also obtains in the case of radicals and biradicals.

Thus one may expect that, if the energies of the excited states of radicals and biradicals are relatively low, the quantum yield of their luminescence should be smaller than for molecules.

## III. THE BENZYL RADICAL

The luminescence of radicals of the benzyl type (the triphenylmethyl radical) was first observed in 1944.[20] This radical was formed chemically in solution in the ether–isopentane–alcohol (EPA) mixture; on cooling the solution to 90 K, the absorption and luminescence spectra of the radical were recorded.

The benzyl radical is the simplest odd alternant aromatic hydrocarbon and its structure has been thoroughly investigated.[21] It is illustrated in Fig. 1*a*. Three of the four electrons of the methyl carbon atom are located in the hybrid $sp^3$ orbitals forming two C–H bonds and one C–C bond; the fourth electron is involved in $\pi$ conjugation.

Numerous theoretical calculations by various methods[22–25] indicate the occurrence of prohibited electronic transitions in the range 400–500 nm (2.5–3 eV) and of allowed transitions in the ultraviolet region of the spectrum at 250–350 nm (3.5–5 eV).

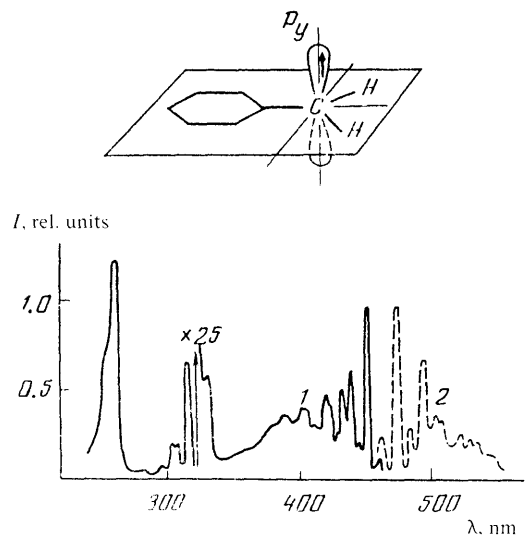



**Figure 1.** *a*) The structure of the benzyl radical; *b*) the excitation (curve *1*) and luminescence (curve *2*) spectra of the benzyl radical in a vitreous solution at 77 K.[41]

The absorption spectrum (the luminescence excitation spectrum) of the benzyl radical (Fig. 1) has three distinct bands in the region of 450, 320, and 250 cm, which correspond to different electronic transitions. The characteristics of these bands are presented in Table 1. The most probable extinction coefficients are $\varepsilon_1 \cong 50$ litre $mol^{-1}$ $cm^{-1}$ in the long-wavelength band, $\varepsilon_2 \cong (1-5) \times 10^3$ litre $mol^{-1}$ $cm^{-1}$ in the region of 320 nm, and $\varepsilon_3 \cong 10^4$ litre $mol^{-1}$ $cm^{-1}$ in the short-wavelength region. The weak absorption band in

the region of 450 nm was first observed in the photolysis of toluene in solution in the isopentane–methylcyclohexane glass at 77 K.[26] It has been noted[27] that the extinction coefficient of the benzyl radical can vary with solvent polarity: with increase of the polarity, the ratio $\varepsilon_{258}/\varepsilon_{318}$ diminishes: at room temperature it is 4.4 in cyclohexane, 3.3 in alcohol, and 2.5 in water.

Table 1. The maxima ($\lambda$, nm) and extinction coefficients ($\varepsilon$, litre mol$^{-1}$ cm$^{-1}$) of the first, second, and third absorption bands of the benzyl radical.

| Matrix | $T$, K | $\lambda_1$ | $\varepsilon_1$ | $\lambda_2$ | $\varepsilon_2$ | $\lambda_3$ | $\varepsilon_3$ | Refs. |
|---|---|---|---|---|---|---|---|---|
| Methanol | 298 | — | — | 318 | 1 500 | — | — | [27] |
| Water | 293 | 450 | 50 | 317.5 | 5 500 | 258 | 14 000 | [28] |
| Alcohols | 298 | — | — | 318 | 1 100 | — | — | [29] |
| Cyclohexane | 293 | — | — | 317 | 12 000 | — | — | [30] |
| Gas phase | 293 | — | — | 305.3 | 10[a] | 253 | — | [31] |
| 3-Methylpentane | 77 | 453 | 30 | 318 | 1 100 | — | — | [32] |
| 3-Methylpentane | 77 | 450 | 68 | 318 | 920 | 250 | 1 900 | [33] |
| 3-Methylpentane | 77 | — | — | 318 | 1 000 | 258 | * | [35] |
| 3-Methylpentane | 77 | — | — | 317.5 | 12 000 | — | — | [37] |
| 2-Methyltetrahydrofuran | 77 | 420 | 400 | 320 | 18 000 | — | — | [34] |
| Ether–isopentane–alcohol | 77 | — | — | 318.2 | 19 200 | — | — | [36] |

* $\varepsilon_2/\varepsilon_3$=4,5.

Table 2. The energies of the long-wavelength 0–0 transition ($E_{00}$) in the benzyl radical.

| $E_{00}$, cm$^{-1}$ | Solvent | State | $T$, K | Refs. |
|---|---|---|---|---|
| 21 805 | — | gas | 293 | [38] |
| 22 324 | — | gas | 293 | [39] |
| 22 001.7 | — | gas | 293 | [46] |
| 22 002 | — | gas | 293 | [42] |
| 22 001.5 | — | gas | 293 | [41] |
| 21 575 | Paraffin | gl | 77 | [26] |
| 21 552 | 3-MP | pc | 77 | [41] |
| 21 647 | MCH | pc | 88 | [43] |
| 21 679 | CP | pc | 88 | [43] |
| 21 685 | MCP | pc | 88 | [43] |
| 21 667 | CH | pc | 77 | [48] |
| 21 662 | CH | pc | 77 | [42] |
| 21 626 | n-Pn | pc | 77 | [44] |
| 22 007 | neon | — | 4.2 | [45] |

Notation: gl = vitreous state (glass), pc = polycrystalline state, 3-MP = 3-methylpentane, MCH = methylcyclohexane, CP = cyclopentane, MCP = methylcyclopentane, CH = cyclohexane, and n-Pn = n-pentane.

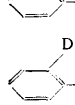
The luminescence of the benzyl radical was first observed in an electric discharge in toluene vapour.[38,39] It was subsequently observed in solutions in glasses[40,41] and in polycrystalline hydrocarbons[42–44] at 77 K and also in a neon matrix at liquid helium temperature.[45] Table 2 presents the energies of the 0–0 transitions of benzyl radicals under different conditions. In the gaseous phase the energy of 22002 cm$^{-1}$ (454.5 nm) appears to be the most likely. The same transition energy has been found also in an inert gas (neon) matrix at 4.2 K. A shift of the 0–0 transition towards lower energies by 300–400 cm$^{-1}$ (~10 nm) has been observed in the condensed phase. Deuteriation of the radical reduces the energy of the 0–0 transition by 90–100 cm$^{-1}$ in both gaseous[48] and condensed[43] phases.

According to theoretical calculations, bands corresponding to two $\pi \rightarrow \pi^*$ electronic transitions, having similar energies but associated with excited electronic levels of different symmetry ($A_2$ and $B_2$), should occur in the long-wavelength part of the spectrum; according to some calculations, the lowest excited level has the $A_2$ symmetry,[49,50] while in other studies the lowest excited state is said to have the $B_2$ symmetry.[24]

A calculation carried out[23] taking into account only singly excited configurations has led to the conclusion that this state has the $B_2$ symmetry; allowance for doubly excited configurations lowers the energy of the states with the $A_2$ symmetry. It is now regarded as established that the lowest excited state has the $A_2$ symmetry both in solid solutions[51] and in the gaseous phase[47,52] and that the splitting between the excited $1^2A_2$ and $2^2B_2$ states is 430–485 cm$^{-1}$ for the benzyl radical and 355–370 cm$^{-1}$ for the perdeuteriobenzyl radical.

Thus the $1^2A_2$–$1^2B_2$ optical transition is responsible for the fluorescence of the benzyl radical. This transition is symmetry-prohibited and the extinction coefficient is approximately 50 litre mol$^{-1}$ cm$^{-1}$ (Table 1) and, when account is taken of the fact that the energy of this transition is ~2.5 eV and that the radical contains relatively few atoms, competition is to be expected between the internal conversion and $D_1 \rightarrow D_0$ fluorescence processes. Experimental data have confirmed this: the fluorescence quantum yield of the benzyl radical is 0.39, while deuteriation increases it to 0.47.[53]

Table 3. The fluorescence lifetimes (μs) of the benzyl radicals in glasses at 77 K and in the gas phase.

| Radical | Matrix | | | | | |
|---|---|---|---|---|---|---|
| | 3-MP (Ref.33) | EPA (Ref.43) | 3-MP (Ref.54) | methanol (Ref.54) | 3-MH (Ref.54) | gas (Ref.56) |
|  | 1.44 | 1.28 | 1.45 | 1.5 | 1.18 | 0.88 |
|  | — | — | 1.80 | — | — | — |
|  | — | — | 1.52 | — | — | — |
|  | — | — | 1 54 | — | — | — |
|  | 1.73 | — | 1.26 | — | — | — |
|  | 3.21 | — | — | — | — | — |
|  | 3.26 | — | 3.22 | — | — | — |
|  | 3.93 | 2.97 | 3.65 | 3.69 | — | 1.34 |

Notation: EPA = ether–isopentane–alcohol and 3-MH = 3-methylhexane; for the significance of the remaining symbols, see the footnote to Table 2.

Table 3 presents the fluorescence lifetimes of the benzyl radical and its deuteriated analogues in glassy solvents at 77 K. These times are of the order of $10^{-6}$ s, which

corresponds to the symmetry-prohibited $\pi \rightarrow \pi^*$ transition. Estimation of the oscillator strength from the formula $f = 1.5\tau_f^{-1}\nu^{-2}$, where $\nu = 22600$ cm$^{-1}$ is the average transition frequency, yields $f = 8 \times 10^{-4}$;[54] the extinction coefficient estimated from this oscillator strength is 68 litre mol$^{-1}$ cm$^{-1}$.[33]

The quartet states of the benzyl radical lie above the lowest excited doublet states. Theoretical calculations lead to the following energies of the lowest quartet states of the benzyl radical: 3.65 eV (29450 cm$^{-1}$),[23] 3.92 eV (31630 cm$^{-1}$),[24] and 3.89 eV (31380 cm$^{-1}$),[25] while the energy of the doublet–doublet transition is 2.67 eV (21550 cm$^{-1}$). The intersystem doublet–quartet conversion $D_{\pi\pi^*}$–$Q_{\pi\pi^*}$ in the benzyl radical cannot compete with the $D$–$D$ internal conversion process whose rate constant exceeds $10^{11}$ s$^{-1}$ for the energy of the transition between the states less than 1 eV; for this reason, the $Q$–$D$ phosphorescence of the benzyl radical has not been observed.

## IV. RADICALS OF THE BENZYL TYPE

This Section deals with the properties of aromatic radicals containing an unpaired electron at the α-carbon atom of an aliphatic substituent. These include radicals arising from the decomposition of alkylbenzenes and their homologues—radicals of the diphenylmethane and triphenylmethane series. Their luminescence-spectroscopic characteristics are presented in Table 4. The unpaired electrons in these radicals participate in π conjugation and their lowest electronically excited states are ππ* states, although they contain an admixture of the σπ* states in the case of nonplanar systems.

**Table 4.** The 0–0 transition energies and the fluorescence lifetimes ($\tau_f$) of radicals of the benzyl type.

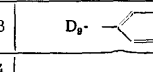
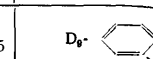
| No. | Radical or initial molecule | $E_{00}$, cm$^{-1}$ | $\tau_f$, s | Solvent | State* | Refs. |
|---|---|---|---|---|---|---|
| 1 |  | 22 002 | — | — | gas | [42] |
| | | 21 662 | — | CH | pc | [42] |
| | | — | 1.45 | 3-MP | gl | [54] |
| | | — | 1.44 | Et | gl | [60] |
| 2 |  | 21 368 | — | Et | gl | [57] |
| | | 21 322 | — | 3-MP | gl | [41] |
| | | 21 345 | — | n-Hx | pc | [58] |
| | | — | 1.19 | 3-MP | gl | [53] |
| | | — | 1.21 | EPA | gl | [53] |
| | | — | 1.33 | Et | gl | [60] |
| 3 |  | — | 2.85 | 3-MP | gl | [33] |
| 4 |  | 20 964 | — | n-Hx | pc | [58] |
| | | 20 942 | — | Et | gl | [57] |
| | | — | 0.79 | EPA | gl | [53] |
| | | — | 0.87 | 3-MP | gl | [33] |
| | | — | 0.87 | Et | gl | [60] |
| 5 |  | — | 1.02 | 3-MP | gl | [33] |
| 6 |  | 21 053 | — | n-Hx | pc | [58] |
| | | 21 008 | — | Et | gl | [57] |
| | | — | 0.79 | 3-MP | gl | [33] |
| | | — | 0.8 | Et | gl | [60] |
| | | — | 0.75 | EPA | gl | [53] |
| 7 |  | 20 963 | — | n-Hx | pc | [58] |
| | | 20 202 | — | Et | gl | [57] |
| | | — | 0.62 | 3-MP | gl | [33] |

**Table 4** (contd.).

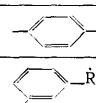
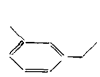
| No. | Radical or initial molecule | $E_{00}$, cm$^{-1}$ | $\tau_f$, s | Solvent | State* | Refs. |
|---|---|---|---|---|---|---|
| 8 |  | 20 222 | — | n-Hx | pc | [58] |
| 9 |  | 21 231 | — | n-Hx | pc | [58] |
| | | 21 008 | — | Et | gl | [57] |
| 10 |  | 20 141 | — | n-Hx | pc | [58] |
| | | 20 121 | — | Et | gl | [57] |
| 11 |  | 21 008 | — | n-Hx | pc | [58] |
| | | 21 231 | — | Et | gl | [57] |
| 12 |  | 20 408 | — | n-Hx | pc | [58] |
| | | 20 408 | 0.54 | 3-MP | gl | [33] |
| | | 20 408 | — | Et | gl | [57] |
| | | — | 0.56 | EPA | gl | [52] |
| | | — | 0.62 | Et | gl | [60] |
| 13 |  | 20 471 | — | n-Hx | pc | [58] |
| | | 20 367 | 0.5 | 3-MP | gl | [33] |
| | | 20 416 | — | pc | pc | [59] |
| | | — | 0.53 | Et | gl | [60] |
| | | — | 0.52 | EPA | gl | [53] |
| | | — | 0.48 | 3-MP | gl | [54] |
| 14 |  | — | 0.59 | 3-MP | gl | [33] |
| 15 |  | 20 964 | — | n-Hx | pc | [58] |
| 16 |  | 20 450 | — | n-Hx | pc | [58] |
| 17 |  | 19 493 | — | n-Hx | pc | [58] |
| 18 |  | 20 450 | — | n-Hx | pc | [58] |
| 19 |  | 19 399 | — | n-Hx | pc | [58] |
| 20 |  | 19 861 | — | n-Hx | pc | [58] |
| | | 19 646 | | | | |
| | | — | 0.35 | IP | gl | [60] |
| | | — | 0.16 | Et | gl | [60] |
| 21 |  | 18 921 | — | n-Hx | pc | [58] |
| | | 18 762 | 0.24 | 3-MP | gl | [33] |
| | | — | 0.16 | Et | gl | [60] |
| 22 |  | 21 400 | — | 3-MP | gl | [61] |
| 23** |  | 21 689 | — | — | gas | [62] |
| 24** |  | 21 460 | — | — | gas | [62] |
| 25** |  | 21 325 | — | — | gas | [62] |
| 26 |  | 21 395 | — | CP | pc | [63] |
| | | 21 400 | — | CH | pc | [63] |
| | | 21 395 | — | MCP | pc | [63] |
| | | 21 377 | — | MCH | pc | [63] |
| 27 |  | 21 144 | — | CP | pc | [63] |
| | | 21 155 | — | CH | pc | [63] |
| | | 21 310 | — | MCP | pc | [63] |
| | | 21 207 | | | | |
| | | 21 155 | | | | |
| | | 21 366 | — | MCH | pc | [63] |
| | | 21 252 | | | | |

**Table 4 (contd.).**

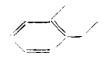
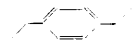
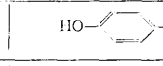
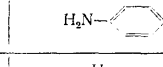
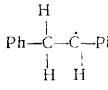
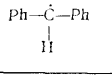
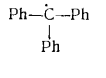
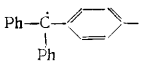
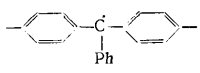
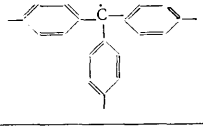
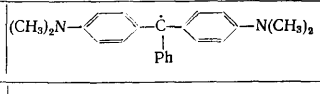
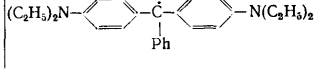
| No. | Radical or initial molecule | $E_{00}$, $cm^{-1}$ | $\tau_f$, s | Solvent | State* | Refs. |
|---|---|---|---|---|---|---|
| 28 |  | 21 115<br>21 105<br>21 162<br>21 070 | —<br>—<br>—<br>— | CP<br>CH<br>MCP | pc<br>pc<br>pc | [63]<br>[63]<br>[63] |
| 29 |  | 20 960<br>20 940<br>20 880<br>20 910<br>20 803<br>20 980<br>20 979 | —<br>—<br>—<br>—<br>—<br>—<br>— | MCP<br>MCH<br>CP<br>n-Hx<br>n-Hp<br>2,2,4-TMP<br>pc | pc<br>pc<br>pc<br>pc<br>pc<br>pc<br>pc | [64]<br>[64]<br>[64]<br>[64]<br>[64]<br>[64]<br>[64] |
| 30 |  | 21 354<br>21 320 | —<br>— | MCP<br>MCH | pc<br>pc | [64]<br>[64] |
| 31 |  | 21 191<br>21 269<br>21 200<br>21 167<br>21 165<br>21 172 | —<br>—<br>—<br>—<br>—<br>— | MCP<br>MCH<br>CH<br>n-Hx<br>n-Hp<br>2,2,4-TMP | pc<br>pc<br>pc<br>pc<br>pc<br>pc | [64]<br>[64]<br>[64]<br>[64]<br>[64]<br>[64] |
| 32 |  | 20 835 | — | 3-MH | gl | [65] |
| 33 |  | 21 053 | — | 3-MH | gl | [65] |
| 34 |  | 24 096 | — | 3-MH | gl | [65] |
| 35 |  | 20 120 | — | Et | gl | [66] |
| 36 |  | 19 050 | — | Et | gl | [66] |
| 37 |  | 21 500 | — | MCH | gl | [67] |
| 38 |  | 19 120<br>—<br>— | —<br>0.44<br>0.41 | Et<br>Et<br>IP | gl<br>gl<br>gl | [68]<br>[60]<br>[69] |
| 39 |  | 19 474<br>19 410<br>19 455<br>19 400<br>19 342<br>19 361<br>19 286<br>—<br>— | —<br>—<br>—<br>—<br>—<br>—<br>—<br>0.28<br>0.33 | MCH + IP<br>EPA<br>Et<br>Tol + EPA<br>Bz<br>n-Hx<br>pc<br>Et<br>IP | gl<br>gl<br>gl<br>pc<br>pc<br>pc<br>pc<br>gl<br>gl | [69]<br>[20]<br>[68]<br>[70]<br>[71]<br>[71]<br>[71]<br>[70]<br>[70] |
| 40 |  | 16 700 | — | Tol + EPA | pc | [70] |
| 41 |  | 16 400 | — | Tol + TEA | pc | [70] |
| 42 |  | 16 400 | — | Tol + TEA | pc | [70] |
| 43 |  | 17 094<br>17 182<br>17 330<br>17 036 | —<br>—<br>—<br>— | Bz<br>n-Hx<br>Et<br>pc | pc<br>pc<br>gl<br>pc | [71]<br>[71]<br>[71]<br>[71] |
| 44 |  | 17 035<br>17 065<br>17 065<br>17 575 | —<br>—<br>—<br>— | Bz<br>n-Hx<br>Et<br>pc | pc<br>pc<br>gl<br>pc | [71]<br>[71]<br>[71]<br>[71] |

**Table 4 (contd.).**

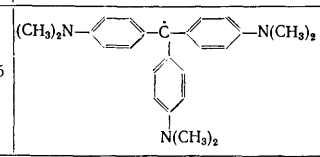
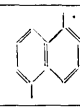
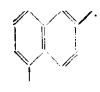
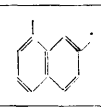
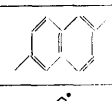
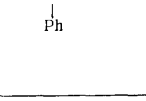
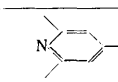
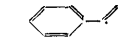
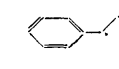
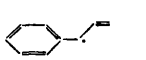
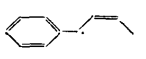
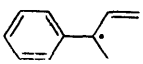
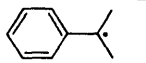
| No. | Radical or initial molecule | $E_{00}$, $cm^{-1}$ | $\tau_f$, s | Solvent | State* | Refs. |
|---|---|---|---|---|---|---|
| 45 |  | 16 640<br>16 680<br>17 035<br>16 530 | —<br>—<br>—<br>— | Bz<br>n-Hx<br>Et<br>pc | pc<br>pc<br>gl<br>pc | [71]<br>[71]<br>[71]<br>[71] |
| 46 |  | 17 012<br>16 593 | —<br>— | n-Hx<br>— | pc<br>gas | [72]<br>[73] |
| 47 |  | 16 722<br>17 017 | —<br>— | n-Hx<br>— | pc<br>gas | [72]<br>[73] |
| 48 |  | 17 010 | — | — | gas | [74] |
| 49 |  | 16 760 | — | — | gas | [74] |
| 50 |  | 16 774 | — | — | gas | [74] |
| 51 |  | 16 648 | — | — | gas | [74] |
| 52 |  | 16 648 | — | — | gas | [74] |
| 53 |  | 16 828 | — | — | gas | [74] |
| 54 |  | 16 816 | — | — | gas | [74] |
| 55 |  | 29 573 | 0.005–0.02 | — | gas | [75] |
| 56 |  | —<br>17 600<br>17 600<br>17 520 | $21\times10^{-3}$<br>$21.1\times10^{-3}$<br>$16.8\times10^{-3}$<br>$2\cdot10^{-3}$ | PVA<br>EPA<br>Et<br>CH | gl<br>gl<br>gl<br>l | [76]<br>[77]<br>[77]<br>[78] |
| 57 |  | 21 360<br>21 900 | —<br>— | argon<br>3-MH | —<br>gl | [159]<br>[159] |
| 58 |  | 21 900 | — | 3-MH | gl | [159] |
| 59 |  | 17 000 | — | n-Pn | pc | [79] |
| 60 |  | 21 100 | — | MCH + IP | gl*** | [80] |
| 61 |  | 21 435 | — | MCH + IP | gl | [160] |

**Table 4** (contd.).

| No. | Radical or initial molecule | $E_{00}$, cm$^{-1}$ | $\tau f$, s | Solvent | State* | Refs. |
|---|---|---|---|---|---|---|
| 62 |  | 18 975 | — | MCH + IP | gl | [160] |
| 63 |  | 18 940 | — | MCH + IP | gl | [160] |
| 64 |  | 19 085 | — | MCH + IP | gl | [160] |
| 65 |  | 21 390 | — | MCH + IP | gl | [160] |

Notation: Et = ethanol, n-Hx = n-hexane, IP = isopentane, n-Hp = n-heptane, TMP = trimethylpentane, Tol = toluene, TEA = triethylamine, Bz = benzene, PVA = poly(vinyl alcohol), and l = liquid state; for the significance of the remaining abbreviations see the footnotes to Tables 2 and 3.

*In the gas phase and for solution No.56 in CH room temperature was used; the temperature for specimens Nos.1–22, 32–47, 56, and 59–66 was 77 K; the temperature for specimen No.57 in argon and No.59 was 20 K; the temperature for specimens Nos.26–31 was 88 K.

**Here R = $CH_3$, $C_2H_5$, or n-$C_3H_7$.

***Thermoluminescence was observed on raising the temperature above 77 K.

It is seen from Table 4 that the introduction of alkyl substituents into the aromatic ring of the benzyl radical reduces the energy of the first excited $D_{\pi\pi^*}$ state; the decrease is 2760 cm$^{-1}$ for hexamethylbenzene. The probability of the radiative transition increases with increase of the number of aliphatic substituents as a consequence of the removal of the symmetry prohibition, which entails an increase of the fluorescence quantum yield[33] and a decrease of the lifetime of the excited state. As for the benzyl radical, the $D_1$–$D_0$ internal conversion process competes with the emission process, which is the reason for the effect of isotope substitution on the fluorescence lifetime.

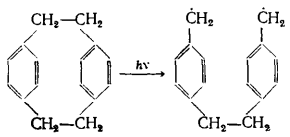
The photolysis of certain compounds (pentamethylbenzene, ethylmethylbenzenes), in solid matrices gives rise to nonequivalent radicals and at least two sets of vibrational bands appear in the luminescence spectrum, while a doublet with a splitting of 100–200 cm$^{-1}$ corresponds to the 0–0 transition (Table 4). However, only one set of vibrational bands is manifested in a gas discharge regardless of the nature of the second alkyl substituent.[62] This suggests that the radical is formed in the discharge as a result of the dissociation of a C–H with minimal energy. The same result has been obtained also in the condensed phase.[63] It has been shown in relation to reactions involving the abstraction of a halogen atom on electron capture in γ-irradiated frozen solutions[61] that, if a radical with an unpaired valence at the β-carbon atom of the alkyl substituent is formed initially, it rearranges to a more stable radical via the dissociation of the α-C–H bond even in a vitreous solution.

An interesting effect of the dissociated halide ion on the luminescence-spectroscopic properties of benzyl type radicals has been observed.[55,57,61,76] A halide ion adjoining the radical induces a bathochromic shift of the spectrum (by 140 cm$^{-1}$ for $Cl^{-1}$), a change in the vibrational structure of the fluorescence spectrum of the radical, and a decrease of the fluorescence lifetime. New bands due to radical–halide ion charge-transfer complex appear in the absorption spectrum in the region of 265, 362, 413, and 500 nm for $F^-$, $Cl^-$, $Br^-$, and $I^-$ respectively. This effect is absent in polar matrices, since the halide ion is solvated by solvent molecules.

The fluorescence of the diphenylmethyl and triphenylmethyl radicals is displaced to the red region relative to the benzyl radical (Table 4) and the energy of the 0–0 transition for the diphenylmethyl radical (19120 cm$^{-1}$) is smaller than for the triphenylmethyl radical (19400 cm$^{-1}$). This is apparently associated with the fact that the diphenylmethyl radical has a structure closer to planarity. It has been noted[70] that methyl substituents in the *para*-position significantly reduce (by 3000 cm$^{-1}$) the energy of the 0–0 transition for triphenylmethyl radicals. This appears doubtful, since the introduction of even the amino-group shifts the 0–0 transition band by a smaller amount (by 2400 cm$^{-1}$).[71] In the benzyl radical the methyl, hydroxy-, and amino-substituents in the *para*-position lower the 0–0 transition energy by 250, 1500, and 2500 cm$^{-1}$ respectively (Table 4).

The luminescence of other radicals of the benzyl type is known only for methylnaphthalenes.[72–74] In the photolysis of methylnaphthalene in n-paraffin matrices at 77 K, a luminescence, attributed to methylnaphthyl radicals, appears in the red region.[72] Luminescence attributed to methylnaphthyl radicals has also been observed in an electric discharge in ethyl- and dimethyl-naphthalene vapours.[73,74] Both in the gas discharge and in the condensed phase, the energy of the 0–0 transition is in the region of approximately 17000 cm$^{-1}$ (~590 nm), but in the case of the gas discharge the 0–0 transition of the α-methylnaphthyl radicals has a lower energy than for the β-methylnaphthyl radical, while in solid n-hexane the opposite effect has been observed. The results of theoretical calculations are also ambiguous.[82,83] It may be that the experimental results do not provide an unambiguous answer owing to the inaccurate identification of the products, since the hydronaphthyl radicals, examined below, may be present in the specimen.

An interesting example is provided by the product of the photolysis of (2,2)-*p*-cyclophane in vitreous solutions,[81] which was formed via the reaction




It can exist in two configurations, one of which corresponds to a biradical (a radical pair) and the other to two benzyl radicals linked by the $-CH_2-CH_2-$ group. Together with the band characteristic of the benzyl radical, a structureless band in the range 500–700 nm, attributed to the emission from the radical pair, appears in its luminescence spectrum. On decrease of the viscosity of the matrix, the intensity of the long-wavelength band diminishes, because the conformational transformations of the photolysis product are facilitated.

Table 4 presents data for the acenaphthyl and α-styryl radicals (Nos.59 and 60). These hydrocarbon radicals are not of the benzyl type, because their unpaired electron occupies the $sp^2$-hybrid orbital of the carbon atom, i.e. is an *n* electron. The lowest excited states of these radicals are therefore $n\pi^*$ states, have a long radiative lifetime,

and their fluorescence quantum yield cannot be high. The luminescence in the range 588–640 nm, manifested in the photolysis of the acenaphthene in n-pentane at 20 K, has been observed[79] and has been attributed to the luminescence of the acenaphthyl radical. A luminescence has been observed[80] which the authors attributed to the α-styryl radical, whose absorption bands are in the region of 320 and 480 nm.[84] However, special investigations[65] failed to confirm these observations. Thus there are at present no reliable data on the luminescence of hydrocarbon radicals from $D_{n\pi^*}$ states owing to its low yield, as in the case of the luminescence observed for the $S_{n\pi^*}$ molecular states.

## V. HYDRO-RADICALS

Hydro-radicals are formed by the addition of a hydrogen atom to the aromatic ring of a π-electron molecule. Such radicals have been investigated in detail by EPR.[85] The luminescence of a hydro-radical was first observed in solid solutions.[86,87]

The simplest hydro-radical is the cyclohexadienyl radical arising following the addition of a hydrogen atom to a benzene molecule, its structure being illustrated in Fig. 2. The cyclohexadienyl radical can be regarded as a polyene chain made up of five carbon atoms. Accordingly, its lowest excited state is of the $D_{\pi\pi^*}$ type and the probability of the long-wavelength electronic transition is high.

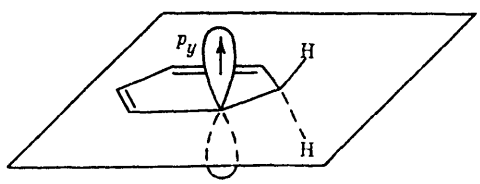
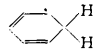
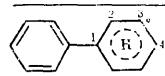
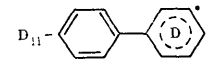
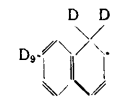
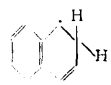
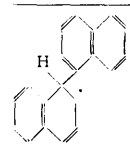
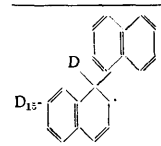



**Figure 2.** The structure of the cyclohexadienyl radical.

The luminescence of the cyclohexadienyl radical was observed after the laser excitation of crystalline benzene subjected to preliminary radiation by fast electrons at liquid helium temperature.[88] Its fluorescence band has undergone a 2500 $cm^{-1}$ bathochromic shift compared with the benzyl radical. In conformity with the fact that the $D_{\pi\pi^*} \to D_0$ transition is allowed, the luminescence lifetime is approximately 2 ns (Table 5). The effect of isotope substitution on the fluorescence lifetime indicates the competition of $D_1$–$D_0$ internal conversion and emission processes; this is consistent with the finding that the transition energy is approximately 2 eV.

The biphenyl and naphthalene molecules contain non-equivalent carbon atoms; for this reason, the hydro-radicals formed by the addition of hydrogen at these positions have different absorption and luminescence spectra. Different 0–0 transition energies of the hydrobiphenyl radical, with maximum differences of 200 $cm^{-1}$, correspond to four different isomers.[89] The 0–0 transition energies of the isomers of the hydrobiphenyl radical have been calculated theoretically,[89] the results being in good agreement with experimental data. The 1-hydrobiphenyl radical has the highest energy of the first excited state. This can be accounted for by the fact that there is no interaction between the benzene rings in this radical.

**Table 5.** The 0–0 transition energies and fluorescence lifetimes of hydro-radicals.

| Radical | $E_{00}$, $cm^{-1}$ | $\tau_f$, ns | Solvent | State | T, K | Refs. |
|---|---|---|---|---|---|---|
|  | 17 902<br>18 127 | 2±1<br>— | Bz<br>cyclohexa-1,4-diene | pc<br>pc | 4.2<br>4.2 | [88]<br>[88] |
|  | 18 041 | 6±1 | Bz-$d_6$ | pc | 4.2 | [88] |
|  | 14 943<br>15 004<br>15 126<br>15 142 | — | biphenyl | cr | 4.2 | [89] |
|  | 15 029<br>15 088<br>15 211<br>15 228 | — | biphenyl-$d_{10}$ | cr | 4.2 | [89] |
|  | 19 530<br>18 557<br>18 530<br>18 484 | —<br>40<br>120 | BA, Et + EE<br>naphthalene<br>naphthalene | gl<br>cr<br>cr | 77<br>4.2<br>77 | [86,87]<br>[90]<br>[91] |
|  | 18 653<br>18 631 | — | naphthalene-$d_8$ | cr | 4.2 | [90] |
|  | 21 460 | — | BA, Et + EE | gl | 77 | [86,87] |
|  | 14 125<br>14 094<br>14 079<br>14 063 | — | naphthalene | cr | 4.2 | [92] |
|  | 14 180<br>14 150<br>14 136<br>14 121 | — | naphthalene-$d_8$ | cr | 4.2 | [92] |

Notation: BA = vitreous boric acid, EE = diethyl ether, and cr = crystal; for the significance of the remaining abbreviations, see the footnotes to Tables 2–4.

In the naphthalene molecule there are two non-equivalent positions to which correspond two isomers: the α- and β-hydronaphthyl radicals,[86,87] differing in the absorption, luminescence, and EPR spectra. A photochromic interconversion of the α- and β-radicals has been observed in solid solutions.[86,87]

In the case of a naphthalene single crystal irradiated by fast electrons, the luminescence of only one α-hydronaphthyl radical was observed. In the crystal field the radical occupies two non-equivalent positions; the splitting between the levels amounts to 27 $cm^{-1}$.[90] Binaphthyl hydro-radicals

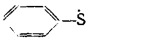
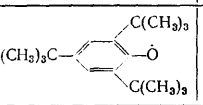
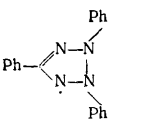
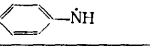
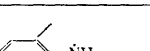
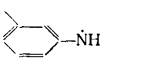
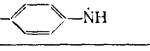
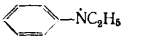
having four non-equivalent positions have also been observed in the single crystal; for this reason four vibrational band progressions are manifested in their fluorescence spectra.

The luminescence properties of a small number of hydroradicals, presented in Table 5, have now been investigated.

## VI. HETERORADICALS

Aromatic radicals having an unpaired electron at a heteroatom (heteroradicals) are widely known in the literature and have been investigated both by EPR and by optical absorption spectroscopy. Many of these radicals are stable[93] but the luminescence properties have been investigated only for four types of heteroradicals; thiophenoxy-, phenoxy-, verdazyl, and anilino-radicals (Table 6).

**Table 6.** The 0–0 transition energies and fluorescence lifetimes of heteroradicals.

| No. | Radical | $E_{00}^{*}$, cm$^{-1}$ | $\tau_f$, ns | Solvent | Refs. |
|---|---|---|---|---|---|
| 1*** |  | 25 000<br>15 650<br>15 650<br>15 650<br>25 000<br>25 000 | —<br>—<br>$(29.3\pm0.5)\cdot10^3$<br>$(51.4\pm0.5)\cdot10^3$<br>$(73\pm5)\cdot10^3$<br>$(60\pm5)\cdot10^3$ | EPA<br>EPA<br>3-MP<br>EPA<br>3-MP<br>EPA | [94]<br>[94]<br>[95]<br>[95]<br>[95]<br>[95] |
| 2 |  | 25 000 | — | Bz | [96] |
| 3 |  | 20 600<br>12 500 | —<br>— | Et<br>Et | [99]<br>[99] |
| 4 |  | 24 400 | 12±2 | EE | [98] |
| 5 |  | 25 000 | — | EE | [98] |
| 6 |  | 24 700 | — | EE | [98] |
| 7 |  | 24 300 | — | EE | [98] |
| 8 |  | 24 000 | 12±2 | EE | [98] |

*The fluorescence band maxima are quoted for No.3; the accuracy of the measurement for Nos.4–8 is to within ±300 cm$^{-1}$.

**Room temperature for No.2 and 77 K (vitreous state) in the other cases.

***Laser generation was achieved with *p*-aminothiophenoxy-radicals (S.Ishizaka and M.Kotani, Chem.Phys.Letters, 1985, 117, 251).

*The thiophenoxy-radical ( the phenylsulphyl radical).* The luminescence of the thiophenoxy-radicals has been investigated after the photolysis of frozen solutions of thiophenol or diphenyl disulphide in EPA or 3-MP at 77 K.[94] A characteristic feature of the luminescence of this radical consists in the fact that emission has been observed in two parts of the spectrum, at 400–500 and 640–700 nm, and is due to two different electronic transitions ($D_2$–$D_0$ and $D_1$–$D_0$). The lifetime of the red fluorescence is 30–50 μs whilst that of the blue fluorescence is 60–70 ps.[95] The opposite shifts of the red and blue fluorescence bands in different solvents show that the long-wavelength fluorescence corresponds to the $D_{n\pi^*}$–$D_0$ transition, while the short-wavelength fluorescence corresponds to the $D_{\pi\pi^*}$–$D_0$ transition. The spectroscopic behaviour of this radical constitutes an instance of the deviation from Kasha's rule, which is rare even for molecules. The deviation is caused by the fact that the rate constant for the $D_2$–$D_1$ internal conversion between the $\pi\pi^*$ and $n\pi^*$ levels is small both as a consequence of the orbital nature of the transition and as a consequence of the relatively large transition energy (1.15 eV).

*The phenoxy-radical.* The luminescence of the 2,4,6-tri-t-butylphenoxy-radical, obtained chemically in solution in benzene, has been observed at room temperature in the range 400–450 nm.[96] However, it is known[97] that, apart from the absorption band in the range 350–400 nm, the phenoxy-radical has a long-wavelength absorption band in the range 500–700 nm and for this reason the fluorescence is apparently caused by a transition of the $\pi\pi^*$ type from the second doublet level. The structure of the phenoxy-radical is illustrated in Fig. 3*a*.

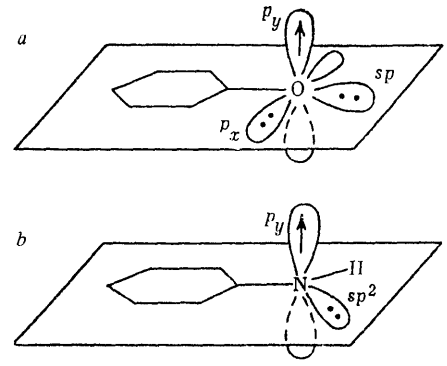



Figure 3. The structure of the phenoxy-radical (*a*) and the phenylaminyl radical (*b*).

*The phenylaminyl radical (the anilino-radical).* The luminescence of the phenylaminyl radical has been observed after the photolysis of aniline in glassy solutions in ether and MCH at 77 K[98] (Fig. 4). The absorption spectrum of this radical has two bands: a weak band in the region of 400 nm and a more intense band in the region of 300 nm.[100] For the sterically hindered 2,4,6-tri-t-butylphenylaminyl radical, obtained photochemically in solution in hexane at room temperature,[101] the extinction coefficients $\varepsilon_{400}$ = 670 litre mol$^{-1}$ cm$^{-1}$ and $\varepsilon_{300}$ = 4700 litre mol$^{-1}$ cm$^{-1}$ have been measured. The short luminescence lifetime of the radical (Table 6) made it possible to assign it to a $D_{\pi\pi^*}$–$D_0$ fluorescence. The phenylaminyl radical is isoelectronic

with the phenoxyradical (Fig. 3*b*), but absorption and emission by the phenylaminyl radical in the long-wavelength region have not so far been observed.

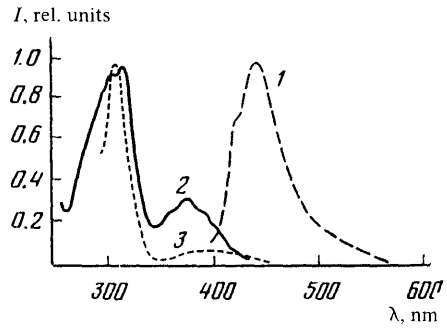



**Figure 4.** The excitation (curve 2) and luminescence (curve 1) spectra of the phenylaminyl radical in ether at 77 K [98] and the absorption spectrum (curve 3) of the phenylaminyl radical in heptane at room temperature.[101]

The phenoxy- and aminyl radicals are isoelectronic with the benzyl radical (cf. Figs. 1 and 3), but their luminescence properties are significantly different (cf. Figs. 1 and 4). This can be explained by the inclination of the axis of the $p_y$ orbital in the heteroradical relative to the plane of the ring or by its strong conjugation with a carbon atom of the ring and the formation of a structure close to one of the quinonoid type.

*The verdazyl radical.* The luminescence of the stable triphenylverdazyl radical (Table 6, No. 3) has been investigated in solution in ethanol, isoctane, diisopropyl ether, benzene, and poly(ethylene glycol) at 77 K.[99] The radical, obtained chemically, has two absorption bands with maxima at 400 and 700 nm, to which correspond two luminescence bands in the region of 485 and 800 nm (in ethanol). In the other solvents enumerated above, the short-wavelength luminescence maxima are at 472, 497, and 478 nm respectively, while in acetonitrile the maximum is at 518 nm.

## VII. RADICAL-IONS

The luminescence of radical-ions was first observed for the radical-cations of triphenylmethane dyes in vitreous solutions at 77 K.[102] The most intense investigations of the luminescence of the radical-ions of aromatic compounds have been carried out recently. The results are presented in Table 7.

*Halogenobenzenes.* The luminescence properties of the radical-cations of halogenobenzenes have been studied in detail in the gas phase. The luminescence spectra were then compared with the photoelectron spectra.

Fig. 5 presents the photoelectron spectrum of 1,2,4-trifluorobenzene on irradiation with light corresponding to the He(I) line.[103] The $\tilde{X}$ band in this spectrum corresponds to the formation of a radical-cation in the ground state, while the $\tilde{A}$, $\tilde{B}$, $\tilde{C}$, etc. bands correspond to excited states of the radical-cation. During photoionisation, the radical-cations are formed in an excited state and their transition to the ground state is accompanied by luminescence. The lowest excited state $\tilde{A}$ is located near $\tilde{X}$ and is due to the splitting of the ground state in asymmetric (with not more than a twofold symmetry axis) halogeno- or alkyl-benzenes. The luminescence (doublet–doublet $\pi \rightarrow \pi^*$ fluorescence) of such radical-cations is observed in the $\tilde{B} \rightarrow (\tilde{X}, \tilde{A})$, $\tilde{C} \rightarrow (\tilde{X}, \tilde{A})$, etc. transitions, but is not observed for the $\tilde{A} \rightarrow \tilde{X}$ transition as a consequence of the smallness of the energy gap. The energies of the electronic levels of certain radical–cations are presented in Fig. 6.[104,106] Using the method based on the coincidences of photoelectrons and luminescence photons,[105] it has now been possible to observe luminescence from the $\tilde{C}$ and $\tilde{D}$ levels and to estimate the lifetimes of the highest electronic states, which proved to be several times shorter than for the $\tilde{B}$ level.

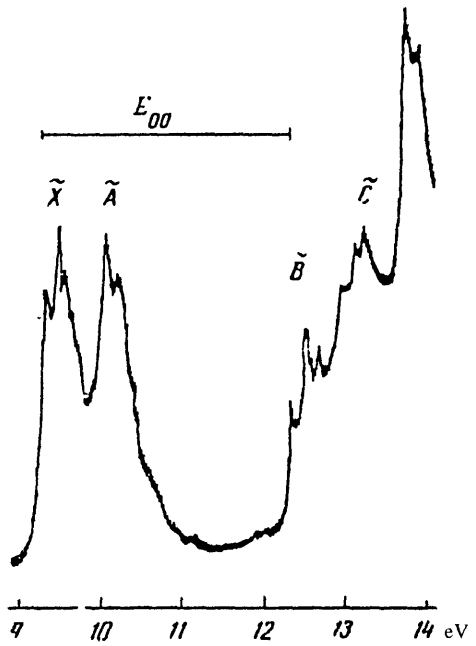



**Figure 5.** Photoelectron spectrum of 1,2,4-trifluorobenzene.[103]

The fluorescence of the radical-cations derived from halogenobenzenes has also been investigated in inert (argon and neon) matrices at temperatures close to liquid helium temperature.[110,111] In solid argon the excitation and luminescence lines of the radical-cations are broader and are displaced towards the red region relative to the neon matrix.[112,113] This is due to the higher energy of the interaction of the radical-cations with the argon atoms than with the neon atoms. The luminescence spectra of the radical-cations obtained in the neon matrix are close to the spectrum in the gas phase. The vibrational structures of the absorption and luminescence are similar, which indicates only a small change in the geometrical parameters of the system on electronic excitation.

Polarisation studies of the fluorescence of the radical-cations in a neon matrix at helium temperatures have been carried out.[114] For molecules with the $D_{6h}$ and $D_{3h}$ symmetries, where the ground state is degenerate, the luminescence is polarised with a degree of polarisation $P = I_{\parallel}/I_{\perp} = 4/3$. For low symmetry radical-cations, for example 1,2,4,5-$C_6H_2F_4^+$, two sets of vibrational bands are observed in the emission spectrum. One set, with a degree of polarisation $P = 3.0$, corresponds to a transition to the lowest non-degenerate state $\tilde{X}^2B_2$. The second system of bands is displaced to the red region and perpendicular polarisation ($P = 0.5$) predominates in it. This system has been attributed to the transition $\tilde{B}^2B_2$–$\tilde{A}^2B_1$.

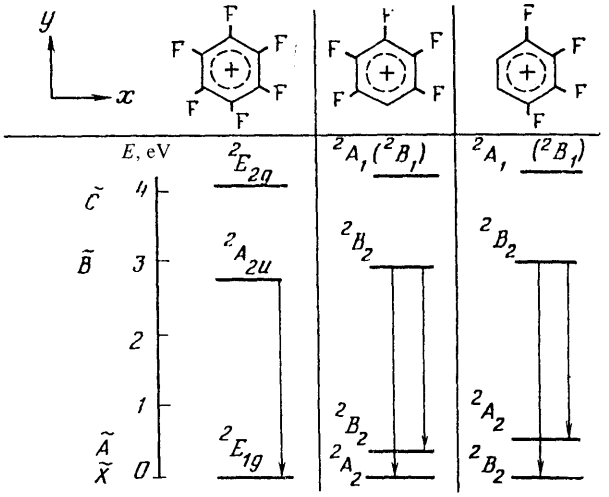


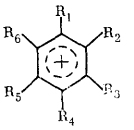

Figure 6. Schematic illustration of the electronic states and the radiative transitions of the radical-cations of fluorobenzenes.[104,106]

The luminescence quantum yield varies from unity in perfluorobenzene to approximately $10^{-2}$ in difluorobenzene, while the luminescence lifetimes amount to tens of nanoseconds, which shows that the transition of the $\pi \rightarrow \pi^*$ type is allowed.[106] Such behaviour of the luminescence yield can be accounted for by the increase of the $D_{\pi\pi^*}$–$D_0$ internal conversion rate constant with increase of the number of C–H oscillators in the system.[13] This is one of the causes of the low luminescence yield of the benzene radical-cation (see below).

The rate constant for the non-radiative decomposition of the excited states increases with increased amount of the vibrational energy in the excited state and with decrease of the transition energy.[105,106] Luminescence investigations have established the following features of the vibrational relaxation in the radical-cations of halogenobenzenes:[114,115] (1) the lifetimes of vibrationally excited states are in the range from 200 ps to less than a picosecond; (2) the rate of relaxation increases with increase in the amount of vibrational energy but not monotonically; (3) the rate of vibrational relaxation increases with decrease in the symmetry of the system. Theoretical studies of the Jahn–Teller effect in symmetrical radical-cations of halogenobenzenes have been made.[117–119]

For a long time it has not been possible to observe the luminescence of the benzene radical-cation. The reason for this is that the lowest excited level has the $^2E_{2g}$ symmetry and the radiative transition $^2E_{2g} \rightarrow {}^2E_{1g}$ is prohibited and non-radiative processes predominate. Luminescence has been observed in an argon matrix at 12 K;[111] it is manifested on laser excitation in the form of three weak peaks at 19770, 19140, and 18290 $cm^{-1}$ (at 19860, 19270, and 18400 $cm^{-1}$ for deuteriobenzene). The luminescence can be accounted for by the fact that in an argon matrix the $^2A_{2u}$ and $^2E_{2g}$ excited levels are inverted, which produces the radiative transition $^2A_{2u} \rightarrow {}^2E_{1g}$. The benzene radical-cations are unstable; on irradiation with light from a mercury lamp, they rapidly decompose and their fluorescence vanishes.

**Table 7.** The 0–0 transition energies and fluorescence lifetimes and quantum yields ($q$) of the radical-cations of substituted benzene derivatives.




| No. | Substituents | $E_{00}$, $cm^{-1}$ | $\tau_f$, ns | $q$ | Solvent | State* | Refs. |
|---|---|---|---|---|---|---|---|
| 1 | $R_1$=$R_2$=$R_3$=$R_4$=$R_5$=$R_6$=H | 19 770 | — | — | Ar | — | [111] |
| 2 | $R_1$=$R_2$=$R_3$=$R_4$=$R_5$=$R_6$=D | 19 860 | — | — | Ar | — | [111] |
| 3 | $R_1$=$R_3$=F, $R_2$=$R_4$=$R_5$=$R_6$=H | —<br>23 230<br>—<br>22 998 | <10<br><6<br><15<br><0.1 | 0.003<br>0.002<br>0.006<br>— | —<br>—<br>—<br>Ne | gas<br>gas<br>gas<br>— | [106]<br>[107]<br>[105]<br>[104] |
| 4 | $R_1$=$R_2$=$R_3$=F, $R_4$=$R_5$=$R_6$=H | 22 460<br>22 288<br>—<br>** | —<br>51±2<br>48±4<br><15 | —<br>—<br>0.74<br>0.11 | —<br>Ne<br>—<br>— | gas<br>–<br>gas<br>gas | [113]<br>[124]<br>[105]<br>[105] |
| 5 | $R_1$=$R_2$=$R_4$=F, $R_3$=$R_5$=$R_6$=H | 24 177<br>24 278<br>24 274<br>— | 10<br>10±2<br>16±5<br>15 | —<br>—<br>0.05<br>0.14 | Ne<br>—<br>—<br>— | —<br>gas<br>gas<br>gas | [124]<br>[107]<br>[104, 106]<br>[105] |
| 6 | $R_1$=$R_3$=$R_5$=F, $R_2$=$R_4$=$R_6$=H | 21 774<br>21 867<br>21 869<br>—<br>21 855 | 53±2<br>58±2<br>57±4<br>59±3<br>— | —<br>—<br>0.87<br>1.0<br>— | Ne<br>—<br>—<br>—<br>— | —<br>gas<br>gas<br>gas<br>gas | [124]<br>[107]<br>[104, 106]<br>[105]<br>[119] |
| 7 | $R_1$=$R_3$=$R_5$=F, $R_2$=$R_4$=$R_6$=D | 21 934<br>21 831<br>— | —<br>—<br>57±2 | —<br>—<br>0.87 | —<br>Ne<br>— | gas<br>–<br>gas | [129]<br>[110]<br>[106 |
| 8 | $R_1$=$R_2$=$R_3$=$R_4$=F, $R_5$=$R_6$=H | 23 192<br>23 277<br>23 292<br>—<br>23 298 | 44±2<br>50±2<br>51±2<br>50±3<br>— | —<br>—<br>0.43<br>0.90<br>— | Ne<br>—<br>—<br>—<br>— | —<br>gas<br>gas<br>gas<br>gas | [104]<br>[107]<br>[104, 106[<br>[105]<br>[113] |
| 9 | $R_1$=$R_3$=$R_4$=$R_5$=F, $R_2$=$R_6$=H | 23 232<br>23 321<br>23 324<br>24 072<br>24 440<br>— | 43±2<br>59±2<br>53±3<br>—<br>—<br>50±3 | —<br>—<br>0.52<br>—<br>—<br>0.99 | Ne<br>—<br>—<br>Ar<br>—<br>— | —<br>gas<br>gas<br>–<br>gas<br>gas | [124]<br>[107]<br>[104, 106]<br>[112]<br>[112]<br>[105] |
| 10 | $R_1$=$R_2$=$R_4$=$R_5$=F, $R_3$=$R_6$=H | 24 358<br>24 438<br>24 443<br>22 903<br>23 321<br>— | 30±2<br>30±2<br>35±3<br>—<br>—<br>32±2 | —<br>—<br>0.21<br>—<br>—<br>0.61 | Ne<br>—<br>—<br>Ar<br>—<br>— | —<br>gas<br>gas<br>–<br>gas<br>gas | [124]<br>[107]<br>[104, 106]<br>[112]<br>[112]<br>[105] |
| 11 | $R_1$=$R_3$=$R_4$=$R_5$=F, $R_3$=$R_6$=D | — | 38±3 | 0.74 | — | gas | [105] |

Table 7 (contd.).

| No. | Substituents | $E_{00}$, $cm^{-1}$ | $\tau_f$, ns | $q$ | Solvent | State* | Refs. |
|---|---|---|---|---|---|---|---|
| 12 | $R_1=R_2=R_3=R_4=R_5=F$, $R_6=H$ | 23 014 | 40±2 | — | Ne | — | [124] |
| | | 33 137 | 47±2 | — | — | gas | [107] |
| | | 23 097 | 51±4 | 0.52 | — | gas | [104, 106] |
| | | 22 810 | — | — | — | — | [112] |
| | | 23 096 | — | — | — | gas | [112] |
| | | — | 48±3 | 0.98 | — | gas | [105] |
| 13 | $R_1=R_2=R_3=R_4=R_5=R_6=F$ | 21 645 | 48±2 | — | — | gas | [107] |
| | | 21 600 | 54±4 | 0.41 | — | gas | [104, 106] |
| | | 21 372 | — | — | Ar | — | [112] |
| | | 21 606 | — | — | — | gas | [112] |
| | | — | 49±3 | 1.0 | — | gas | [105] |
| | | 21 557 | 42 | — | Ne | — | [124] |
| | | 21 617 | — | — | — | gas | [128] |
| 14 | $R_1$=Cl, $R_2=R_4=R_6=H$, $R_3=R_5=F$ | 19 220 | 6 | — | — | gas | [125] |
| 15 | $R_1$=Cl, $R_2=R_3=R_6=F$, $R_4=R_5=H$ | 21 080 | 21±3 | — | — | gas | [125] |
| 16 | $R_1$=Cl, $R_2=R_4=R_5=F$, $R_3=R_6=H$ | 21 640 | 6 | — | — | gas | [125] |
| 17 | $R_1$=Cl, $R_2=R_3=R_4=R_5=F$, $R_6=H$ | 20 600 | 27±2 | — | — | gas | [125] |
| 18 | $R_1$=Cl, $R_2=R_3=R_5=R_6=F$, $R_4=H$ | — | 52±2 | — | — | gas | [125] |
| 19 | $R_1=R_3$=Cl, $R_2=R_5=R_6=H$, $R_4=F$ | 19 940 | 8±2 | — | — | gas | [125] |
| 20 | $R_1=R_3$=Cl, $R_2$=F, $R_4=R_5=R_6=H$ | 18 540 | 14±3 | — | — | gas | [125] |
| 21 | $R_1=R_3$=Cl, $R_2=R_4=R_6=H$, $R_5$=F | 17 205 | 8±2 | — | — | gas | [125] |
| 22 | $R_1=R_4$=Cl, $R_2$=F, $R_3=R_5=R_6=H$ | 19 620 | 6 | — | — | gas | [125] |
| 23 | $R_1=R_3$=Cl, $R_2=R_4$=F, $R_5=R_6=H$ | 19 855 | 29±3 | — | — | gas | [125] |
| 24 | $R_1=R_3$=Cl, $R_2=R_5$=F, $R_3=R_6=H$ | 18 940 | 38±2 | — | — | gas | [125] |
| 25 | $R_1=R_4$=Cl, $R_2=R_5$=F, $R_3=R_6=H$ | 19 955 | 6 | — | — | gas | [125] |
| 26 | $R_1=R_3$=Cl, $R_2=R_4=R_6$=F, $R_5=H$ | 20 035 | 38±3 | — | — | gas | [125] |
| 27 | $R_1=R_3=R_5$=Cl, $R_2$=F, $R_4=R_6=H$ | 17 080 | 22±2 | — | — | gas | [125] |
| 28 | $R_1$=Cl, $R_2=R_3=R_4=R_5=R_6$=F | 19 990 | 43±3 | — | — | gas | [125] |
| | | 19 914 | 37±2 | — | Ne | — | [124] |
| 29 | $R_1=R_3=R_5$=Cl, $R_2=R_4=R_6=H$ | 15 265 | 19 | — | Ne | — | [124] |
| | | 15 398 | — | — | — | — | [129] |
| 30 | $R_1=R_3=R_5$=Cl, $R_2=R_4=R_6$=F | 16 948 | — | — | — | gas | [127] |
| | | 16 636 | — | — | Ar | — | [126] |
| | | 16 785 | 29±5 | — | Ne | — | [126] |
| | | 16 950 | 34±3 | — | — | gas | [125] |
| | | — | 35±3 | 0.66 | — | gas | [131] |
| 31 | $R_1=R_3=R_5$=Cl, $R_2=R_4=R_6$=D | 15 270 | — | — | Ne | — | [110] |
| 32 | $R_1=R_2=R_4=R_5$=Cl, $R_3$=F, $R_6=H$ | 17 135 | — | — | — | gas | [125] |
| 33 | $R_1=R_3=R_4=R_5$=F, $R_2=R_6$=Br | 14 745 | — | — | — | gas | [116] |
| 34 | $R_1=R_4$=Br, $R_2=R_3=R_5=R_6$=F | 14 870 | — | — | — | gas | [116] |
| 35 | $R_1=R_3=R_5$=Br, $R_2=R_4=R_6$=F | 13 510 | — | — | — | gas | [116] |
| | | — | 6 | 0.52 | — | gas | [131] |
| 36 | $R_1$=$CH_3$, $R_2=R_4=R_6$=F, $R_3=R_5=H$ | 22 636 | 41±2 | — | Ne | — | [124] |
| 37 | $R_1$=$CH_3$, $R_2=R_3=R_5=R_6$=F, $R_4$=H | 23 360 | 43±2 | — | — | gas | [108] |

Table 7 (contd.).

| No. | Substituents | $E_{00}$, $cm^{-1}$ | $\tau_f$, ns | $q$ | Solvent | State* | Refs. |
|---|---|---|---|---|---|---|---|
| 38 | $R_1$=$CH_3$, $R_2=R_3=R_4=R_5=R_6$=F | 21 750 | 40±2 | — | Ne | — | [124] |
| | | — | 43±2 | — | — | gas | [108] |
| 39 | $R_1$=$CH_3$, $R_2=R_5$=Cl, $R_3=R_4=R_6=H$ | 19 690 | 6 | — | — | gas | [108] |
| 40 | $R_1$=$CH_3$, $R_2=R_4=R_6=H$, $R_3=R_5$=Cl | 17 490 | 10±2 | — | — | gas | [108] |
| 41 | $R_1$=$CF_3$, $R_2=R_3=R_5=R_6$=F | 23 030 | — | — | Ne | — | [113] |
| | | — | 45±2 | — | — | gas | [108] |
| 42 | $R_1=R_4$=$CF_3$, $R_2=R_3=R_5=R_6$=F | — | 11±3 | — | — | gas | [108] |
| 43 | $R_1=R_3=R_5$=$CH_3$, $R_2=R_6=H$, $R_4$=F | 21 468 | 0.01 | — | Ne | — | [124] |
| 44 | $R_1=R_3=R_5$=$CH_3$, $R_2=R_6$=F, $R_4$=H | 22 086 | 27±2 | — | Ne | — | [124] |
| 45 | $R_1=R_3=R_5$=$CH_3$, $R_2=R_4=R_6$=F | 21 140 | 35±2 | — | Ne | — | [124] |
| | | — | 37±2 | — | — | gas | [108] |
| 46 | $R_1$=OH, $R_2=R_3$=F, $R_3=R_4=R_6=H$ | 23 785 | 13±3 | — | — | gas | [109] |
| 47 | $R_1$=OH, $R_2=R_4=R_6$=H, $R_3=R_5$=F | 21 990 | 36±4 | — | — | gas | [109] |
| | | 21 908 | — | — | Ne | | [133] |
| 48 | $R_1$=OH, $R_2=R_3=R_4$=F, $R_5=R_6=H$ | 23 790 | 26±3 | — | — | gas | [109] |
| 49 | $R_1$=OH, $R_2=R_4=R_5$=F, $R_3=R_6=H$ | 24 240 | 6 | — | — | gas | [109] |
| 50 | $R_1$=OH, $R_2=R_3=R_5=R_6$=F, $R_4$=H | 21 860 | 41±4 | — | — | gas | [109] |
| | | 21 798 | 40 | — | Ne | — | [133] |
| 51 | $R_1$=OH, $R_2=R_3=R_4=R_5=R_6$=F | 22 410 | 33±3 | — | — | gas | [109] |
| | | 22 407 | 32±2 | — | Ne | — | [124, 130] |
| 52 | $R_1$=CN, $R_2=R_3=R_4=R_5=R_6$=F | — | 6 | — | — | gas | [108] |
| 53 | $R_1$=$NH_2$, $R_2=R_3=R_4=R_5=R_6$=F | *** | — | — | — | gas | [108] |
| 54 | $R_1$=$NO_2$, $R_2=R_3=R_4=R_5=R_6$=F | | | | | | |
| 55 | $R_1$=$OCH_3$, $R_2=R_3=R_4=R_5=R_6$=F | | | | | | |
| 56 | $R_1$=$COCH_3$, $R_2=R_3=R_4=R_5=R_6$=F | | | | | | |
| 57 | $R_1$=CHO, $R_2=R_3=R_4=R_5=R_6$=F | | | | | | |

*Liquid helium temperature obtained in inert gas (Ar and Ne) matrices and room temperature was used in the gas phase.

**Fluorescence of the $\tilde{C} \rightarrow \tilde{X}$ transition.

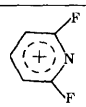
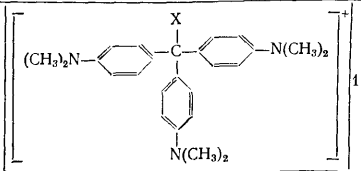
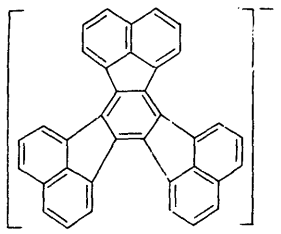
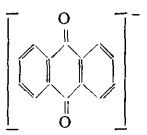
***Only luminescence was noted for the radical-cations Nos. 53–57.

*Other substituted benzenes.* Apart from halogenobenzenes, the luminescence of radical-cations of halogenated alkylbenzenes, alkylphenols, and alkylbenzonitrile derivatives has now been investigated (Table 7). In addition, the luminescence in the gas phase of the radical-cations of pentafluorobenzene with the following substituents has also been reported: $NH_2$, $NO_2$, $OCH_3$, COOH, and CHO,[108] although spectroscopic data have not been presented. The energies of the 0–0 transitions for the radical-cations of phenols and methyl-substituted benzenes lie in the same range as for halogenobenzenes and the luminescence lifetimes are also similar; there are no quantum yield data. The methyl and hydroxy-substituents influence the spectroscopic characteristics similarly to a fluorine atom but their effect on non-radiative processes is apparently significantly

different. It has been noted[108] that the gas-phase luminescence of the radical-cations of xylenes and pentamethylbenzenes has not been observed. The same communication quotes a list of 42 aromatic compounds for which the luminescence of radical-cations could not be observed in the range 300–850 nm on ionisation of these compounds in the gas phase with an electron beam having an energy of 20–40 eV.

*Complex aromatic molecules.* The fluorescence of the radical-cations of molecules more complex than those of substituted benzenes has been observed for the leuco-base of Crystal Violet (Table 8). The study of two-step photoionisation and photodissociation reactions of aromatic amines in solutions in ethanol at 77 K led to the observation[102] of the luminescence of the photolysis product, which was modified on replacement of the methyl hydrogen atom in the leuco-base by the OH or CN group. The luminescence band with a maximum near 17000 $cm^{-1}$ and the absorption band at 21000 $cm^{-1}$, which the authors[102] attributed to the radical-cation of the leuco-base of Crystal Violet, proved to be the most stable under these conditions.

Table 8. The 0–0 transition energies and fluorescence lifetimes and quantum yields of the radical-ions of aromatic compounds.

| No. | Radical-ion | $E_{00}$, $cm^{-1}$ | $\tau$, s | $q$ | Solvent** | Refs. |
|---|---|---|---|---|---|---|
| 1 |  | 27 158 | — | — | Ne | [132] |
| 2 |  | 17000* | — | — | Et | [102] |
| 3 |  | 15 700<br>14 500 | $10^{-11}$<br>$2.6\cdot10^{-3}$ | $10^{-3}$<br>$10^{-4}$ | 2-MTHF<br>2-MTHF | [120]<br>[121] |
| 4 |  | 20 000 | — | — | Et + KOH | [122] |

Notation: 2-MTHF = 2-methyltetrahydrofuran; for the significance of the remaining abbreviations, see the footnotes to Tables 2–5.

*The fluorescence maximum is indicated.
**The helium temperature was used for specimen No.1, while in the remaining cases the temperature was 77 K.

Interesting studies of the luminescence properties of the decacyclene radical-anion (Table 8, No.3) have been carried out.[120,121] The phosphorescence from a quartet level, i.e. a radiative quartet–doublet transition, was observed for the first time in these investigations. The decacyclene radical-anion absorbs intensely in the infrared with a maximum at 4950 $cm^{-1}$ and absorbs in the visible region at 16500 $cm^{-1}$. If a solution of decacyclene radical-anions in 2-methyltetrahydrofuran (in which neutral molecules are also present) at 77 K is excited with light at a wavelength longer than that of the singlet–singlet absorption of the neutral molecule ($E_{S_1}$ = 21 400 $cm^{-1}$), then fluorescence attributed to the $D_2$–$D_0$ transition and phosphorescence with $\tau_p = 2.6 \times 10^{-3}$ s, attributed to the $Q_1$–$D_0$ transition of the radical-anion, are observed. The electronic levels of the decacyclene radical-anion are illustrated schematically in Fig.7 and the main spectroscopic characteristics are listed in Table 8 (No.3).

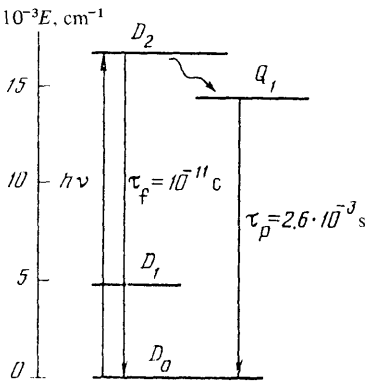



Figure 7. Schematic illustration of the electronic states of the decacyclene radical-anion.[120,121]

The luminescence of the radical-anions has also been observed for anthraquinone.[122] In ethanol to which a 0.1 M KOH solution has been added, anthraquinone is reduced to the radical-anion having a characteristic absorption at 480 nm. A broad luminescence band with a maximum at 540 nm (at room temperature) has been attributed to the fluorescence of the anthraquinone radical-anion, since its excitation spectrum coincided with the absorption spectrum, while the absorption and fluorescence spectra exhibit mirror symmetry. On reducing the temperature to 77 K, the bands undergo a bathochromic shift, which may be associated with dimerisation.

Attention should be drawn to a study[123] whose authors investigated the luminescence of an anthracene solution in a 1:2 mixture of acetic and sulphuric acids. In such a solution it is possible to photoinduce anthracene radical-cations having absorption bands at 315, 352, and 720 nm and an EPR spectrum, which vanish in the dark in the course of several minutes. The luminescence in the range 550–600 nm, excited by light with a wavelength shorter than 500 nm, is correlated with this behaviour. This emission has been attributed to the fluorescence of the anthracene radical-cation. Such interpretation requires further confirmation, because, as noted by the authors

themselves,[123] it has been found that the luminescence spectrum depends on the exciting light wavelength, which means that either different products emit or charge-transfer complexes or exciplexes are formed, so it cannot be regarded as unambiguously established that the observed emission is due to the anthracene radical-cations.

## VIII. BIRADICALS

*Carbenes.* The luminescence of aromatic biradical species was observed for the first time for diphenylcarbene,[134] whose structure is illustrated in Fig. 8*a*.[135] It has been shown by EPR[136] that the benzene rings are located in the same plane and that the angle between them is 140–150°. The unpaired electrons are present in two orbitals, one of which is located in the plane of the rings, while the other is at right angles to this plane. The spins of these electrons are parallel; the ground state of carbene is a triplet, which has been demonstrated by EPR also for other aromatic carbenes.[137] The unpaired electron present in the 2*p* orbital perpendicular to the molecular plane is conjugated to the π-electron system and for this reason the luminescence-spectroscopic properties of diphenylcarbene should resemble those of the benzyl and diphenylmethyl radicals. Indeed the absorption spectrum of diphenylcarbene contains a weak band in the region of 450 nm and a more intense band in the region of 300 nm,[134,138,139] whose extinction coefficients have been estimated[140] as $\varepsilon_{301}$ = 2500 litre mol$^{-1}$ cm$^{-1}$ and $\varepsilon_{465}$ = 300 litre mol$^{-1}$ cm$^{-1}$. The long-wavelength absorption is polarised along the line connecting the benzene rings[139] so that one can claim that they correspond to the $T_0 \rightarrow T_{\pi\pi^*}$ transition.

The luminescence spectrum of diphenylcarbene is presented in Fig. 8*a* (curve 2). Since the carbene has a triplet ground state, the observed luminescence has been identified as triplet–triplet fluorescence, which has been confirmed by the mirror symmetry of the absorption spectrum (or the excitation spectrum) and the luminescence spectrum and also by the short luminescence lifetime.[134,135,140]

The electron present in the orbital in the molecular plane is an *n* electron and can participate in $n \rightarrow \pi^*$ transitions. In the spectra of aromatic aldehydes and ketones the absorption bands corresponding to the $n \rightarrow \pi^*$ transitions are in the region of 300–400 nm[1–4] and the extinction coefficient corresponding to the $n \rightarrow \pi^*$ transitions is small (~100 litre mol$^{-1}$ cm$^{-1}$). In the spectra of carbenes the bands corresponding to the $n \rightarrow \pi^*$ transitions are apparently in the same range 300–400 nm, but the absorption is relatively weak and is masked by the more intense absorption corresponding to the $\pi \rightarrow \pi^*$ transitions, which determine the luminescence properties of aromatic carbenes.

It has not yet been discovered what influence is exerted on the spectroscopic properties of carbenes by the lowest singlet state having the same electronic configuration as the ground triplet state. Direct photolysis of diazodiphenylmethane results in the formation of diphenylcarbene in the lowest singlet state, from which it passes to the ground triplet state after a period of approximately 10$^{-11}$ s.[141] The energy gap $S_1$–$T_0$, estimated from the equilibrium constants of the chemical reactions of diphenylcarbene, is only 3–5 kcal mol$^{-1}$[(1 – 2) × 10$^3$ cm$^{-1}$].[141–143] For such a small energy gap, it is naturally impossible to expect an appreciable yield of the phosphorescence corresponding to the $S_1$–$T_0$ transition. Theoretical estimation of the $S_1$–$T_0$ gap leads to 10–20 kcal mol$^{-1}$ [(3.5–7) × 10$^3$ cm$^{-1}$].[144] Such a large discrepancy between the experimental and theoretical values is associated both with the approximate character of the quantum-chemical methods used in the calculation and the fact that the experimental values do not correspond to the equilibrium configuration of the system.

The lifetime of diphenylcarbene at the $T_{\pi\pi^*}$ excited level at 77 K is approximately 10$^{-7}$ s; the introduction of heavy atoms (in the form of ethyl iodide) into the solution does

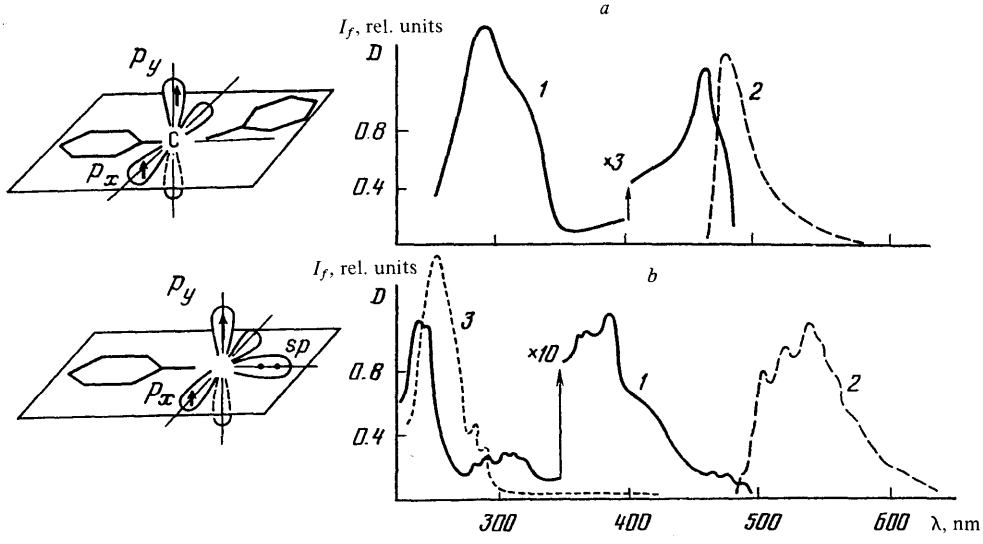



**Figure 8.** a) The structure of the excitation (curve *1*) and the luminescence (curve *2*) spectra of diphenylcarbene;[134,135] b) the structure and the absorption (curve *1*) and luminescence (curve *2*) spectra of phenylnitrene and the absorption spectrum of the initial phenyl azide (curve *3*).[149]

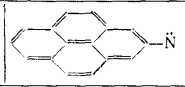
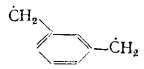
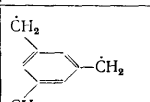
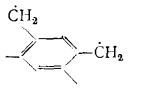
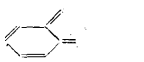
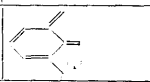
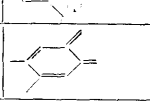
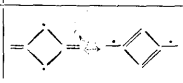
not entail sharp changes in this value. Hence one may conclude that the probability of the intersystem crossing $T_{\pi\pi^*} \rightarrow S_1$ is small because the energy gap is approximately 2.5 eV and the conversion does not compete with the luminescence.

Fluorescence has been observed also for many *para*-substituted dephenylcarbenes (Table 9). If the substituent is a nitro-group, then there is no fluorescence.[135,158] This finding can be accounted for by the fact that in nitro-derivatives the $S_{n\pi^*}$ states lie below the $T_{\pi\pi^*}$ state and the $T_{\pi\pi^*}$–$S_{n\pi^*}$ conversion suppresses the fluorescence, similarly to the situation which obtains in molecules as a consequence of the $S_{\pi\pi^*}$–$T_{n\pi^*}$ conversion.[2-5]

Table 9. The 0–0 transition energies and the fluorescence lifetimes and quantum yields of the biradicals of aromatic compounds at 77 K.

| No. | Biradical | $E_{00}$, $cm^{-1}$ | $\tau_f$, ns | $q$ | Solvent | State | Refs. |
|---|---|---|---|---|---|---|---|
| 1 | Ph–C̈–Ph | 20 830 | — | — | MCH, EPA | gl | [134, 135] |
| | | — | 108 | — | MC | gl | [145] |
| | | — | 87 | 0.25 | Et | gl | [145] |
| | | — | 72 | — | Et + EtI | gl | [145] |
| | | — | 4* | — | 3-MP | gl | [143] |
| | | 20 750 | 123 | 0.2 | MCH | gl | [152] |
| | | 20 830 | 113.6 | 0.2 | Et | gl | [158] |
| | | 20 660 | 94.3 | 0.32 | Et + EtI | gl | [158] |
| | | 21 410 | 73.3 | — | MCH + EtI | gl | [158] |
| 2 | Ph–C̈–C₆H₄–Cl | 20 530 | — | — | MCH | gl | [135] |
| 3 | Ph–C̈–C₆H₄–Br | 20 490 | — | — | MCH | gl | [135] |
| 4 | Ph–C̈–C₆H₄–CH₃ | 20 530 | — | — | MCH | gl | [135] |
| 5 | Ph–C̈–C₆H₄–OCH₃ | 20 200 | — | — | MCH | gl | [135] |
| | | 20 450 | 77.1 | 0.27 | MCH | gl | [158] |
| | | 20 200 | 79.4 | 0.14 | Et | gl | [158] |
| | | 20 325 | 74.5 | 0.17 | Et + EtI | gl | [158] |
| | | 20 280 | 76.4 | — | MCH + EtI | gl | [158] |
| 6 | Ph–C̈–C₆H₄–CN | 19 600 | 84 | 0.61 | MCH | gl | [158] |
| | | 19 600 | 74.6 | 0.78 | Et | gl | [158] |
| | | 19 570 | 66.4 | 0.19 | Et + EtI | gl | [158] |
| | | 19 400 | 74.8 | — | MCH + EtI | gl | [158] |
| | | 19 600 | 91.7 | 0.51 | MCH-*d* | gl | [158] |
| 7 | Ph–C̈–Ph | 18 020 | — | — | MCH | gl | [135] |
| | | 17 540 | — | — | EE + IA | gl | [146] |
| 8 | CH₃O–C₆H₄–C̈–C₆H₄–OCH₃ | 19 725 | — | — | MCH | gl | [135] |
| | | 19 840 | 66.8 | 0.47 | MCH | gl | [158] |
| | | 19 880 | 72.1 | 0.27 | Et | gl | [138] |
| 9 | Br–C₆H₄–C̈–C₆H₄–Br | 20 080 | 11.4 | 0.02 | MCH | gl | [158] |
| | | 20 040 | 11.4 | 0.06 | Et | gl | [158] |
| | | 20 120 | 11.7 | 0.05 | Et + EtI | gl | [158] |
| 10 | NC–C₆H₄–C̈–C₆H₄–CN | 19 000 | 69.5 | 0.38 | MCH | gl | [158] |
| | | 18 870 | 65.9 | 0.23 | Et | gl | [158] |
| | | 18 870 | 59.6 | 0.2 | Et + EtI | gl | [158] |
| 11 | Ph–C̈–C₆H₄–C₆H₄–C̈–Ph | 17 240 | — | — | Et | gl | [146] |
| 12 | C₆H₄–N̈ | 20 570 | — | — | Et | gl | [149, 153] |
| 13 | H₃C–C₆H₄–N̈ | 20 970 | — | — | Et | gl | [149, 153] |
| 14 | H₂N–C₆H₄–N̈ | 20 330 | | — | Et | gl | [149] |
| 15 | H₃CO–C₆H₄–N̈ | 21 460 | — | — | Et | gl | [149] |

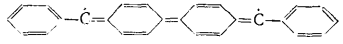
Table 9 (contd.).

| No. | Biradical | $E_{00}$, $cm^{-1}$ | $\tau_f$, ns | $q$ | Solvent | State | Refs. |
|---|---|---|---|---|---|---|---|
| 16 | Ph–C₆H₃–N̈ | 18 800 | 2 | — | Et + EE | gl | [149, 157] |
| 17 | N̈–C₆H₄–C₆H₄–N̈ | 16 220 | 18 | — | Et + EE | gl | [157] |
| 18 | N̈–C₆H₄–CH₂–C₆H₄–N̈ | 20 820 | — | — | Et | gl | [153] |
| 19 | Ph–CH(Ph)–C₆H₄–N̈ | 21 300 | — | — | Et | gl | [153] |
| 20 | N̈–C₆H₄–CH(Ph)–C₆H₄–N̈ | 20 570 | — | — | Et | gl | [153] |
| 21 |  | 23 000 | 7* | — | Bz | l | [151] |
| 22 |  | 22 370 | — | — | n-Pn | pc | [155] |
| 23 |  | 22 100 | — | — | n-Pn | pc | [155] |
| 24 |  | 22 430 | — | — | n-Pn | pc | [155] |
| 25 |  | 24 130 | — | — | n-Pn | pc | [155] |
| 26 |  | 24 100 | — | — | n-Pn | pc | [155] |
| 27 |  | 23 850 | — | — | n-Pn | pc | [155] |
| 28 |  | 19 685 | — | — | MTHF | gl | [161] |

Notation: EtI = ethyl iodide, MCH-*d* = deuteriated MCH, and IA = isopropyl alcohol; for the significance of the remaining abbreviations, see the footnotes to Tables 2–8.

*Room temperature.

Dicarbene (Table 9, No.11), whose luminescence has been observed,[146] constitutes a special case. Formally it should have a sextet ground state, but, as a consequence of π-conjugation, it passes to a triplet state, which corresponds to a quinonoid structure:



For this reason, the luminescence of dicarbene is also $T_{\pi\pi^*} \rightarrow T_0$ fluorescence.

*Nitrenes.* The electronic structure of nitrenes resembles that of carbenes (Fig. 8*b*). The unpaired electrons are in two 2*p* orbitals, one of which ($p_x$) is in the molecular plane, while the other ($p_y$) is perpendicular to this plane. Furthermore, a nitrene contains an unpaired electron pair which

occupies a hybrid *sp* orbital located also in the molecular plane. Aromatic nitrenes are usually formed on photolysis of light-sensitive compounds such as azides and their chemical and certain spectroscopic properties have therefore been surveyed in a number of reviews and monographs,[147,148] but the luminescence properties of nitrenes have been investigated only recently.

The absorption spectrum of phenylnitrene, obtained on photolysis of phenyl azide in a solid solution at 77 K, is illustrated in Fig. 8*b*.[149] As in the spectrum of the benzyl radical, three bands are observed: an intense band in the region of 240 nm, a less intense one in the region of 300 nm, and a weak band in the region of 350–450 nm. As in carbenes, absorption bands in the range 300–400 nm, masked by the absorption due to the $\pi-\pi^*$ transitions, should correspond to the $n \rightarrow \pi^*$ transitions from the $p_x$ and *sp* orbitals. Theoretical estimates of the transition energies in phenylnitrene[150] describe fairly satisfactorily the experimental absorption spectrum.[149–151]

The luminescence spectrum of phenylnitrene is represented by curve *2* in Fig. 8*b*. The fact that the luminescence is due to the corresponding nitrenes has been confirmed by the agreement between the dynamics of the behaviour of the absorption and luminescence spectra, the mirror symmetry of the spectra, and the coincidence of the luminescence excitation spectrum with the absorption spectrum of nitrene.[149] The luminescence lifetime is approximately $10^{-8}$ s and, when account is taken of the fact that nitrenes have a triplet ground state,[141] one may conclude that the observed emission represents the triplet–triplet fluorescence of nitrenes.

Phenylnitrene is isoelectronic with the benzyl radical (cf. Figs. 1 and 8) and their luminescence-spectroscopic properties are very similar, which significantly distinguishes phenylnitrenes from the phenoxy- and aminyl heteroradicals.

The addition of the methyl group to the *para*-position causes a hypsochromic and not a bathochromic shift of the band corresponding to the 0–0 transition in phenylnitrene, in contrast to aromatic molecules. This phenomenon had been observed earlier for radical-ions and had been explained by the inductive effect.[152] The inductive effect is associated with the redistribution of the electron density in the excited state: when it increases at the site of the addition of the substituent, the transition energy rises, i.e. the hypsochromic shift of the 0–0 transition is observed. When alkyl substituents are introduced into simple aromatic molecules, the hyperconjugation effect, which always leads to a bathochromic shift of the absorption band, usually predominates. In this case the inductive effect predominates in the nitrene.

The luminescence properties of aromatic nitrenes are presented in Table 9; in many respects they resemble those of carbenes. Phenylnitrenes with alkyl electron-donating substituents fluoresce, while electron-accepting substituents (the nitro- and acetyl group) quench the fluorescence of nitrene.[149] As in the case of carbenes, the presence of *n* electrons in the substituent gives rise to the possibility of an intense $T_{\pi\pi^*}-S_{n\pi^*}$ conversion and leads to the quenching of the fluorescence.

It follows from Table 9 that a dinitrene with strong conjugation between the nitrene groups (4,4-dinitrenobiphenyl, Table 9, No. 17) also fluoresces, which is due to its biradical quinonoid structure. In the case of weakly conjugated systems, such as triphenylmethanes, the individual molecular fragments make independent contributions to the absorption spectra. However, the fluorescence quantum yield of dinitrenotriphenylmethane (Table 9, No. 20) is an order of magnitude lower than for the mononitrene (Table 9, No. 19), while the fluorescence of trinitrenotriphenylmethane has not been observed at all.[153] This can be explained both by the mutual quenching of the fluorescence due to the individual fragments, analogous to concentration-induced quenching, and by the formation of states with higher multiplicity.

*Xylylenes.* Xylylenes constitute yet another class of biradical species for which luminescence has been observed.[154,155] The photolysis of methylated benzenes in MCH at 77 K [154] led to the observation of the luminescence of the product in the range 400–440 nm, which differs from the luminescence of benzyl radicals and was attributed to *ortho*- and *meta*-xylylenes (such products did not appear for toluene and *p*-xylene). Subsequently xylylenes were synthesised chemically and their luminescence, whose characteristics are presented in Table 9 (Nos. 22–27), was investigated.[155] It is noteworthy that only *meta*-xylylene and its methyl derivatives (Table 9, Nos. 22–24) are true biradical species, while *ortho*-xylylenes (or *para*-xylylenes) have the configuration shown in Table 9 (Nos. 25–27). According to theoretical calculations,[155,156] *meta*-xylylenes have a triplet lowest state so that the observed luminescence can be attributed to triplet–triplet fluorescence. Theoretical estimates of the transition energy agree well with experimental data.[155]

The triplet–triplet fluorescence of the biradical benzene isomer 2,4-dimethylenecyclobutane-1,3-diyl, obtained by the photolysis of an azo-compound, has been observed.[161] This biradical is unstable even at 77 K and decomposes spontaneously; its concentration diminishes by a factor of two over a period of 30 h.

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The studies of the luminescence-spectroscopic properties of the radical products of aromatic compounds have shown that all the rules of the luminescence-spectroscopic systematic treatment developed in recent years for molecular systems[1–5] are applicable to them. Apart from the general selection rules as regards multiplicity and symmetry, account must be taken of the influence of the orbital nature of the excited states in the radiative and non-radiative transitions. The characteristics of the structure of certain radical compounds and the development of modern research methods (laser excitation, accumulation of spectra) made it possible to observe interesting phenomena in the luminescence spectra; quartet–doublet phosphorescence, the Jahn–Teller effect, fluorescence from the highest excited states, laser generation based on the fluorescence of radicals, and vibrational structure in luminescence spectra. The luminescence of radicals of the benzyl type has been most fully investigated and described in the literature; the luminescence of radical-ions of complex aromatic systems, such as naphthalene, biphenyl, etc., as well as the luminescence properties of the heteroradicals have been studied to a much lesser extent.

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# Nucleophilic Substitution Reactions. Modern Ideas About the Mechanism and Reactivity

M.V.Bazilevskii, S.G.Koldobskii, and V.A.Tikhomirov

The mechanism of $S_N2$ reactions is discussed on the basis of gas-phase experimental data and quantum-chemical calculations: the energy relations, stereochemistry, and the form of the potential energy surface. The results of modern kinetic measurements and calculations are presented. The experimental data for the reactions in solution are discussed at the level of qualitative quantum-chemical concepts. The causes of the strong influence of the solvent on the kinetics of these reactions are analysed and the empirical correlations between the kinetic and thermodynamic characteristics and the link between the correlations and modern theoretical ideas are examined.
The bibliography includes 134 references.

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## I. INTRODUCTION

During the last fifteen years, the ideas about the mechanism of nucleophilic substitution in aliphatic compounds have changed beyond recognition. Previous concepts have been revised as a result of studies on the kinetics of gas-phase $S_N2$ reactions with the aid of new mass-spectrometric methods, especially after the experimental results have been confirmed by quantitative quantum-chemical calculations. It was found that the potential energy surface (PES) profile for these reactions is much more complex than had been suggested previously and the mechanisms corresponding to it do not fit within the simplest kinetic schemes which have been generally accepted. The strong influence of the solvent on these reactions has become evident. The mechanism of $S_N2$ processes in a polar medium is much closer to previous schemes than the mechanism of the gas-phase reactions. Elementary theoretical considerations as regards reactivity which ignore fully or almost fully the influence of the medium have paradoxically proved to be applicable only to reactions in a polar solvent, since only such $S_N2$ reactions have the usual PES profile.

In the present review an attempt has been made to summarise and treat systematically the advances in recent years. The familiar nucleophilic substitution reactions have become the subject of the latest experimental and theoretical studies. The principles of the corresponding approaches and research methods are examined in the present review in fair detail. Furthermore, the methods used in the kinetic interpretation of mass-spectrometric experiments, the problems of the theory of chemical reactions in polar media, the correlation between kinetic and thermodynamic characteristics in terms of the Marcus equation, and certain other features of modern theoretical chemistry are also discussed.

## II. THEORETICAL RESEARCH METHODS

### 1. Quantum-Chemical Calculations

Exhaustive information about the mechanism of the reaction of a chemical system can be obtained by calculating the PES. Within the framework of the activated complex theory, it is sufficient to find the geometrical configurations of the minimum corresponding to the reactants and the saddle point corresponding to the transition state (TS) of the reaction and then to estimate the height of the potential barrier from the difference between their absolute energies. In the case of a complex mechanism, one has to investigate complex PES with several minima and saddle points, whereupon the TS with the minimum energy usually corresponds to the preferred reaction pathway. More detailed investigations of PES involve the calculation of reaction pathways, i.e. of multidimensional curves in the internal coordinate space in which energy minima are attained in all the sections orthogonal with respect to their direction. Finally, for simple systems calculations of the dynamics of the movement of the representative point in the PES, classical or quantum, are feasible. This level of theoretical analysis is higher than that involving the calculation of the rate constants in terms of the activated complex theory.

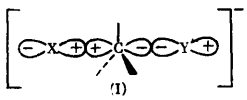
Both semiempirical and non-empirical quantum-chemical methods are used at present for the calculation of the PES. The semiempirical procedures (for example, CNDO/2, MINDO/3, MNDO, etc.) require a moderate expenditure of computer time and are frequently used in studies on complex reactions. Unfortunately they are not immune to uncontrollable errors, which are sometimes serious. In particular the standard semiempirical methods are unsuitable for the calculation of the saddle points of the simplest $S_N2$ reactions.

The non-empirical self-consistent field methods (for example, STO-3G, 3-21G, 4-31G, 6-311G, etc.) are much more laborious (in the incomplete list of non-empirical methods quoted above, the size of the basis set, the labour involved in the calculation, and the quality of the latter increase in the order in which the methods are listed). It has come to be assumed that calculations by the 3-21G or 4-31G method are sufficient for the determination of the geometry of stationary points. In order to achieve reliable energy estimates, it is necessary to expand the basis set and also to take into account electronic correlation. The latter improvement implies going beyond the framework of the self-consistent field procedure. Among the methods whereby correlations can be taken into account, which have been applied successfully to $S_N2$ reactions, mention should be made of the CEPA-PNO scheme (the approximation of interacting electron pairs).

### 2. Qualitative Methods of the Reactivity Theory

The traditional approach, in which the geometrical structures of the transition and initial states are postulated on the basis of intuitive considerations (the validity of the choice of the model can be checked in principle by calculating the PES for the simplest cases), is widely used. For models specified in this way, an elementary quantum-chemical assessment is made of the energy relations, i.e. of the tendency towards a change in the height of the potential barriers in the reaction series.

As an example, we shall consider a model for the TS of an $S_N2$ reaction at a saturated carbon atom. It has the structure (I):



(I)

where X is the nucleophile and Y the leaving group. It is assumed that the atoms X, C, and Y are located on the same axis, which is at right angles to the plane of the trigonal system of the bonds involving the carbon atom. The main element of the electronic structure of such TS is a delocalised three-centre four-electron system made up of three *p* orbitals, which overlap in phase, as shown in Scheme (I). For this system, it is possible to carry out an elementary calculation by the Hückel method or to apply the perturbation theory to the interaction, assuming that the substrate–nucleophile bond (C.X) is much weaker than the "intramolecular" bond C–Y (which is hardly justified). According to the perturbation theory, only the interactions between the occupied and unoccupied molecular orbitals (MO) of the reactants contribute to the energy. Its simplest version, the method of frontier orbitals (FMO), takes into account the contribution to the interaction energy only from a single pair: the highest occupied orbital of the nucleophile (HOMO)—the lowest unoccupied orbital of the substrate (LUMO). Thus it is sometimes possible to predict or explain the characteristics of the variation of the reactivity in reaction series.

In order to analyse the energy of the interaction in the TS, the latter is sometimes subdivided into a series of contributions (several versions of such subdivision are known): Coulombic ($E_{coul}$), polarisation ($E_{pol}$), charge transfer or delocalisation ($E_{ct}$), exchange repulsion ($E_{ex,rep}$), exchange ($E_{exch}$), and dispersion ($E_{disp}$):

$$E = E_{coul} + E_{pol} + E_{ct} + E_{ex,rep} + E_{exch} + E_{disp}. \quad (1)$$

Some of these quantities are combined in a single term. The interaction energy can be calculated by Eqn.(1) using fairly sophisticated quantum-mechanical methods—semiempirical or non-empirical.

### 3. Correlations

In the present review we shall examine only certain aspects of the application of correlations to nuclephilic substitution reactions, namely those for which it is possible to associate the relations with more fundamental approaches. Equations which are strictly speaking empirical can be often derived from a qualitative quantum-chemical analysis or from general geometrical considerations concerning the structure of multidimensional PES. Such derivations sometimes follow simply from the outward similarity of the equations and expansions of the molecular orbital perturbation theory as in the case of linear correlations of the Hammett type. In other cases the considerations are not so trivial. This applies to the Marcus equation, which is now a subject of a vigorous discussion in connection with exchange reactions to which the $S_N2$ reactions belong.

## III. SUBSTITUTION REACTIONS AT A SATURATED CARBON ATOM

### 1. Stereochemical Specificity

The stereochemistry of $S_N2$ reactions has been investigated theoretically already in the course of 50 years at a wide variety of levels: ranging from simple electrostatic

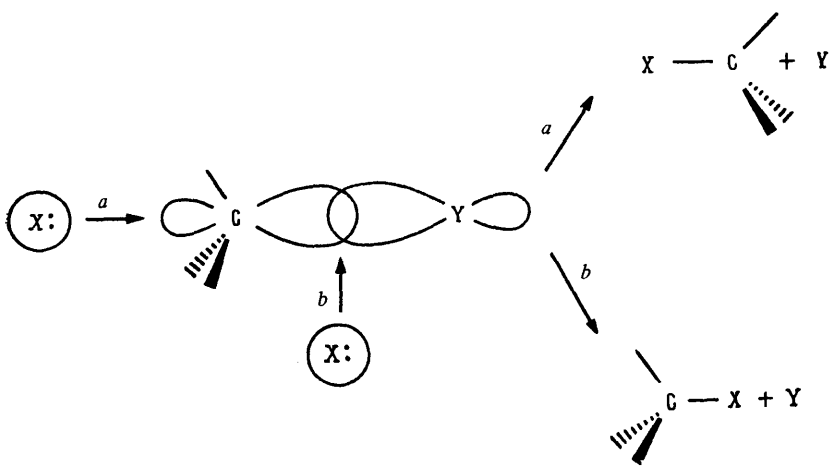



**Figure 1.** The rear (*a*) and frontal (*b*) attack in reactions of the $S_N2$ type.

estimates to modern semiempirical[1-7] and non-empirical[8-13] quantum-chemical calculations. Two directions of attack on the saturated substrate by the nucleophile X, differing in the relative disposition of X and of the leaving group Y, are distinguished (Fig.1): the rear direction, where X attacks the substrate from the side opposite to that of Y, and the frontal direction, where X attacks the substrate from the side of Y. Stereochemically different products correspond to these reaction pathways. Attack from the rear leads to the inversion of configuration (Walden inversion), while frontal attack results in the retention of configuration at the central atom of the substrate.

In the case of a saturated carbon atom, it has been established theoretically that the reaction with inversion of configuration is preferred Thus the search for the TS in the $H^- + CH_4$ system by the STO-3G method without symmetry-dependent limitations led to a configuration with $D_{3h}$ symmetry[13] (Fig.2). The analysis of the form of the MO calculated by the CNDO/2 method for the $F^- + CH_3F$, $H^- + CH_4$, and $NH_3 + CH_3F$ reactions[2] also leads to the conclusion that the configuration is inverted. Analysis of the components of the total energy, calculated by a semiempirical method[3,4] for the $Cl^- + CH_3Cl$ system, shows that the Coulombic and exchange contributions of expansion (1) favour inversion and that the Coulombic component predominates over long distances. The delocalisation contribution is relatively small over long distances but becomes significant when the reactants approach one another and attack from the rear is then also favoured.

Experiment confirms that inversion of configuration is always observed in reactions of the $S_N2$ type at a saturated carbon atom. This fact has been firmly established for reactions both in solution and in the gas phase. In the first gas-phase experiments,[17] it was already shown that the nucleophilic reaction of $Cl^-$ with *cis*- and *trans*-4-bromocyclohexanols takes place with inversion. The stereochemistry of substitution in positively charged intermediates under the influence of water in the gas phase has been investigated by the ion–cyclotron resonance (ICR) method.[18] The substitution takes place via the $S_N2$ mechanism to the extent of 64–98% (depending on the substrate) with inversion of configuration at the carbon atom.

The simplest three-centre four-electron model can be used to compare the electronic structures of the TS corresponding to the rear and frontal attack. The open-chain TS model for attack from the rear was indicated above in Scheme (I). The cyclic TS illustrated in Fig.3 corresponds to frontal attack. The open-chain and cyclic TS structures differ by too many parameters to enable comparison of their energy relations, even at the qualitative level, to be made. However, for each TS it is possible to analyse the conditions favouring the given stereochemical direction of the reaction. For example, the factors which increase the probability of frontal attack can be discovered by the qualitative analysis of the relative stability of the cyclic TS.[7,10,19] We shall examine these considerations in greater detail as a typical example of a qualitative approach to the MO theory. A similar treatment of the open-chain TS is described below.

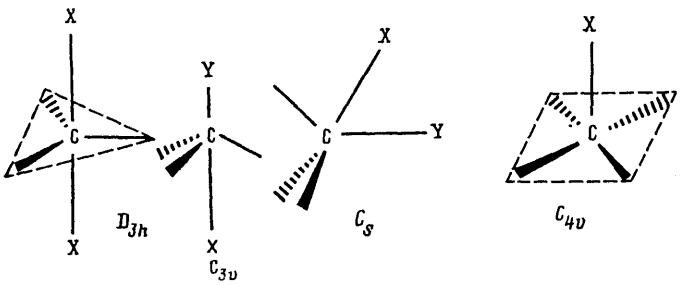



Figure 2. The possible configurations of the TS in $S_N2$ reactions.

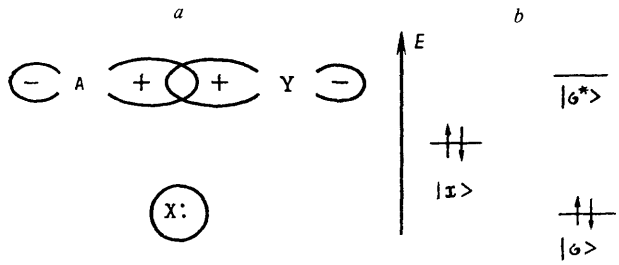



Figure 3. Schematic illustration of the three-centre cyclic TS in reactions of the $S_N2$ type (*a*) and the disposition of the energy levels (*b*).

Direct calculations have shown that the difference between the TS energies for the rear and frontal attack is sufficiently large to assume that the inversion of configuration at the saturated carbon atom is preferred (Table 1 and Fig.2). A high symmetry of the TS corresponding to inversion obtains only if the nucleophile and the leaving group are monatomic anions. For polyatomic nucleophiles and leaving groups and also for asymmetrically substituted substrates, the conclusion that the configuration is inverted remains but the symmetry of the TS is distorted to a greater or lesser extent.[14-16] According to a non-empirical calculation,[14] the angle α(C–X–Y) for X, Y = HO, HOO, $NH_2$, CN, SH, $OCH_3$, or $OC_2H_3$ deviates from 180° by an amount up to 4°. For example, in the $[FCH_3OF]^-$ system the angle α(F–C–O) = 176°, while in the $[HOOCH_3OOH]^-$ system we have α(O–C–O) = 182.4°. In the presence of a methyl substituent at the carbon atom of the substrate, α(X–C–Y) = 150°.[16]

We introduce the following notation: $|x\rangle$ is the HOMO (or AO) of the nucleophile X and $|a\rangle$ and $|y\rangle$ are the AO of the central atom A of the substrate and of the leaving group Y (Fig.3) contributing most to the LUMO $|\sigma^*\rangle$ of the substrate:

$$|\sigma^*\rangle = (|a\rangle - \lambda|y\rangle)(1+\lambda^2)^{-1/2} \cong |a\rangle - \lambda|y\rangle \,. \qquad (2)$$

Within the framework of perturbation theory, the stabilisation of the TS is determined by the interaction of the HOMO $|x\rangle$ of the nucleophile and the LUMO $|\sigma^*\rangle$ of the substrate. The matrix elements of the Hamiltonian *h* will be designated as follows:

$$\langle a|h|a\rangle = \alpha_a; \quad \langle x|h|x\rangle = \alpha_x; \quad \langle y|h|y\rangle = \alpha_y;$$
$$\langle a|h|y\rangle = \beta_{ay}; \quad \langle a|h|x\rangle = \beta_{ax}; \quad \langle x|h|y\rangle = \beta_{xy} \,.$$

It is assumed that they satisfy the relations

$$\alpha_x, \alpha_y \ll \alpha_a < 0; \quad 0 < \lambda \simeq \beta_{ay}/(\alpha_y - \alpha_a) \ll 1; \quad 0 < \lambda' \cong \beta_{ay}/(\alpha_x - \alpha_a) \ll 1. \qquad (3)$$

This means that the electronegativity of the central atom A is much smaller than the electronegativity of the nucleophile X and of the leaving group Y and that on the energy scale the differences between the electronegativities are large compared with the strength of the corresponding bond.

The energy of interaction of the orbitals $|x\rangle$ and $|\sigma^*\rangle$ is

$$\Delta E = 2\langle x|h|\sigma^*\rangle/(\langle x|h|x\rangle - \langle\sigma^*|h|\sigma^*\rangle) < 0 \ .$$

When the higher powers of the small quantities $\lambda$ and $\lambda'$ are neglected, the above expression reduces to

$$\Delta E \simeq -2(\beta_{ax}^2 - 2\lambda\beta_{ax}\beta_{xy})/(\alpha_a - \alpha_x) \ . \qquad (4)$$

It follows from Eqn.(4) that the decrease of the quantity $\lambda$ stabilises the TS. According to Eqn.(3), $\lambda$ (the contribution of the AO $|y\rangle$ to the LUMO $|\sigma^*\rangle$ of the substrate) diminishes with increase of $\alpha_a$ and with decrease of $\alpha_y$. Consequently decrease of the electronegativity of the central atom and increase of that of the leaving group promote frontal attack. This is confirmed by direct calculations and by experiments on nucleophilic substitution at a silicon atom, which is less electronegative than a carbon atom. Calculations of the TS energies for different configurations have shown that, although frontal attack on the silicon atom is energetically less favourable than attack from the rear, it is so to a lesser extent than for a carbon substrate (Table 1). Whereas reactions of the $S_N2$ type at a saturated carbon atom always proceed with inversion, in substitution at a silicon atom configuration is retained[21-24] (in this case frontal attack is preferable to attack from the rear, although the mechanism in the given instance differs from $S_N2$).

Table 1. The relative TS energies with inversion ($D_{3h}$, $C_{3v}$) and retention ($C_s$, $C_{4v}$) of configuration.

| System | $E$, kcal mol$^{-1}$ | | | | Method (basis set) | Refs. |
|---|---|---|---|---|---|---|
| | $C_{3v}$ | $D_{3h}$ | $C_s$ | $C_{4v}$ | | |
| $CH_5^-$ | — | 0 | 56.8 | 54.3 | (7.3/3) → [4.2/2] | [8] |
| $CH_5^-$ | — | 0 | 54.5 | 54.5 | two-exponential function, minimal Slater basis set | [9] |
| $CH_6^-$ | — | 0 | 15 | — | PNDO | [1] |
| $CH_3F_2^-$ | — | 0 | 56.4 | — | 4-31G | [12] |
| $CH_3(CN)_2^-$ | — | 0 | 15 | — | MNDO | [6] |
| $SiH_4F^-$ | 0 | — | 9 | — | STO-3G | [19] |
| $SiH_4Cl^-$ | 0 | — | 33.6 | — | STO-3G | [19] |
| $SiH_5^-$ | — | 0 | — | 2.9 | (12.9/5) → [6.4/2] | [20] |

The increase of the electronegativity of Y within the limits of a single Group of the Periodic System (on replacement of Cl by F or of SR by OR) also favours retention of configuration.[19,24] Furthermore, analysis of the denominator in Eqn.(4) makes it possible to understand the effect of electronegativity of the nucleophile. The conclusion that an increase of $\alpha_x$ facilitates frontal attack is apparently indirectly confirmed by the dependence of the stereochemical specificity of certain $S_N2$ reactions in aprotic solvents on the hardness of the nucleophile.[24] Finally, the inclusion of the central atom of the substrate in the strained cyclopropane ring favours retention of configuration. This result, obtained by calculation using the extended Hückel method (EHM),[7,10] can be explained qualitatively by the fact that the corresponding change in the degree of hybridisation diminishes $\lambda$ by diminishing the absolute value of $\beta_{ay}$. We may note that, even for the reaction with cyclobutane, a similar EHM calculation[5,10] predicts inversion in agreement with a non-empirical calculation[11] and experiment.[25]

The elementary considerations presented above are not faultless even within the framework of the simplest model employed. It is sufficient to point out that a change in the nature of A, X, and Y should influence not only the corresponding quantity $\alpha$ but also $\beta$ in Eqn.(3) or (4) (for example, via a change in the A–X and A–Y bond lengths). In discussing the role of the electronegativity of the atom A, no account was taken of the effect of $\alpha_a$ in the denominator of Eqn.(4), the result of which is the opposite of that of the effect of $\lambda$. Steric effects can be excluded in by no means all the examples examined. Finally, one should consider simultaneously how the above factors influence the stability of the alternative open-chain TS.

## 2. The Mechanism of the Gas-Phase Reactions

Fig. 4 illustrates the complex PES profile along the reaction coordinate of the reaction

$$X^- + CH_3Y \rightarrow XCH_3 + Y^- \ . \qquad (5)$$

It is now generally accepted that the mechanism of the simplest gas-phase reactions (5) is described by a two-well potential curve. The minima correspond to the prereaction complex $[X^-.CH_3Y]$ and the postreaction complex $[XCH_3.Y^-]$ with highly asymmetric structures and localised charges. The bonds represented by dots are mainly electrostatic in nature: the corresponding internuclear distance is still too large for the formation of strong covalent bonds. The bonds in the $CH_3Y$ and $XCH_3$ molecules which enter into the composition of the corresponding complexes are almost undistorted and are largely covalent. The conversion of the first complex into the second proceeds via the saddle point on the PES, to which corresponds the TS $[XCH_3Y]^-$ with a more or less symmetrical structure and a delocalised charge.

The order of magnitude of the stability of the electrostatic complexes can be estimated for the energy of the ion–dipole interaction over the distance corresponding to the sum of the van der Waals radii of the corresponding atoms. Estimates in the range $U \cong 10$–$20$ kcal mol$^{-1}$ are thus obtained. The formation of ion–molecule complexes has been established in a number of gas-phase experiments.[26-31] Their measured formation energies agree with the above estimate. Thus the bond energy of the complex $Cl^-.CH_3CN$ is 16 kcal mol$^{-1}$,[27] while those of the complexes $Hal^-.CH_3Hal$ range from 8.6 to 14.4 kcal mol$^{-1}$.[28-30] The non-equivalence of the X and Y atoms in symmetrical systems (X = Y = Cl) has been demonstrated by isotopic analysis of the reaction products:

$$[^{35}Cl \cdot CH_3^{37}Cl]^- + CH_3CF_3 \rightarrow [^{35}Cl \cdot CH_3CF_3] + CH_3^{37}Cl \ ,$$

where one of the reactants was the complex of the $^{35}Cl^-$ anion with the $CH_3^{37}Cl$ molecule prepared beforehand.[31]

The complexes are apparently not formed in polar solvents. At any rate, liquid-phase experiments provide no evidence for their formation. Up to the beginning of the 1970's, kinetic studies of reactions of type (5) were performed exclusively in the liquid phase and no considerations indicating the possibility of complex mechanisms were put forward. The first convincing piece of evidence was obtained in the theoretical calculation by Dedieu and

Veillard.[32] The main result of this study was the prediction of a two-well PES profile for reaction (5) with X, Y = H, F.

Kinetic studies of gas-phase reactions (5) using the mass-spectrometric technique involving afterglow in a stream,[33–36] the ICR method,[17,37–41] and the pulsating electron beam method[42] yielded final evidence in support of the view that they have a complex mechanism. Approximately 100 kinetic constants have now been measured for such reactions. Table 2 lists the rate constants $k$ for the $X^- + CH_3Y$ reactions; the data for reactions with substituted substrates $CR^1R^2R^3$ are not included. The constants $k$ measured by the afterflow in a stream method are systematically higher than those obtained by the ICR method. The determination of the parameters of a two-well PES from the results of a kinetic experiment presents serious difficulties. Two different procedures for the estimation of the activation barrier $\Delta E$ (Fig. 4), based on different hypotheses concerning the reaction mechanism, were used in Table 2. The Arrhenius equation, in which the pre-exponential factor represents the collision frequency, was employed in the first of these.[36] The large number of $\Delta E$ values close to zero, supporting a complex PES profile, is striking: the reactions for which $\Delta E < 0$ also fell within the group. The second estimate[39–41] is based on the Kassel–Marcus theory (RRKM); for this model, $\Delta E < 0$.

Table 2. The experimental rate constants $k$ ($cm^3$ molecule$^{-1}$ $s^{-1}$), the efficiencies $f$, and the enthalpies $Q_{XY}$ (kcal $mol^{-1}$) of the gas-phase reactions $X^- + CH_3Y \rightarrow XCH_3 + Y^-$ as well as estimates of $\Delta E$ and $E_{XY}$ (kcal $mol^{-1}$) (Fig. 4).

| X | $k \cdot 10^9$ | $f$ | $-Q_{XY}$ | $\Delta E$ | $E_{XY}$ | Refs. |
|---|---|---|---|---|---|---|
| | | | Y=F | | | |
| O | 1.1 | 0.48 | 27 | — | — | [36] |
| CHF | 0.41 | 0.23 | — | — | — | [36] |
| $CH_3NH$ | 0.05 | 0.03 | 43 | 2.1 | — | [36] |
| OH | 0.025 | 0.011 | 18 | 2.7 | — | [36] |
| $NH_2$ | 0.0176 | 0.0076 | 32 | 2.9 | — | [36] |
| H | 0.015 | 0.0020 | 56 | 3.7 | — | [36] |
| $CH_3O$ | 0.014 | 0.0074 | 23 | 2.9 | — | [36] |
| CN | ⩽0.003 | ⩽0.002 | 4 | ⩾3.8 | — | [36] |
| C | ⩽0.002 | ⩽0.0008 | 25 | ⩾4.2 | — | [36] |
| $C_2$ | ⩽0.002 | ⩽0.001 | 5 | ⩾4.1 | — | [36] |
| $CH_3S$ | ⩽0.001 | ⩽0.0006 | 4 | ⩾4.3 | — | [36] |
| CCH | ⩽0.0003 | ⩽0.0002 | 34 | ⩾4.5 | — | [36] |
| | | | Y=Cl | | | |
| H | 3.0 | 0.35 | 88 | 0.62 | — | [36] |
| OH | 1.6 | 0.68 | 48 | — | — | [39] |
| OH | 1.5 | 0.62 | 50 | 0.28 | — | [36] |
| F | 0.80 | 0.35 | 29 | — | — | [39] |
| F | 0.58 | 0.25 | 28 | —(0.9—3.2) | 8.1—5.8 | [41] |
| F | 1.9 | 0.83 | 32 | 0.1 | — | [36] |
| O | 1.7 | 0.71 | 59 | — | — | [36] |
| $CH_3NH$ | 1.7 | 0.85 | 75 | 0.1 | — | [36] |
| $NH_2$ | 1.5 | 0.63 | 64 | 0.3 | — | [36] |
| $CH_3O$ | 0.49 | 0.25 | 39 | — | — | [39] |
| $CH_3O$ | 0.60 | 0.30 | 42 | —(3.1—7.2) | 5.9—1.8 | [41] |
| $CH_3O$ | 1.3 | 0.68 | 55 | 0.23 | — | [36] |
| $C_2H_5O$ | 1.3 | 0.29 | — | — | — | [33] |
| $(CH_3)_3CHO$ | 1.1 | 0.26 | — | — | — | [33] |
| $C_6H_5$ | 0.87 | 0.22 | — | — | — | [33] |
| t-$C_4H_9$-$C_6H_4$ | 0.80 | 0.22 | — | — | — | [33] |
| $CH_2Cl$ | 0.51 | 0.30 | — | — | — | [36] |
| C | 0.30 | 0.11 | 57 | 1.3 | — | [36] |
| t-$C_4H_9$ | 0.16 | 0.10 | 35 | —(2.4—4.7) | 6.6—4.3 | [41] |
| t-$C_4H_9$ | 0.80 | 0.20 | — | — | — | [33] |
| $CH_3S$ | 0.078 | 0.045 | 31 | — | — | [39] |
| $CH_3S$ | 0.11 | 0.065 | 36 | 1.6 | — | [36] |
| $CD_3S$ | 0.052 | 0.03 | 29 | —(1.3—4.0) | 7.7—5.0 | [41] |
| HCC | 0.052 | 0.024 | 51 | —(0.8—4.2) | 8.2—4.8 | [41] |
| HCC | 0.13 | 0.062 | 66 | 1.6 | — | [36] |
| S | 0.030 | 0.016 | 24 | 2.4 | — | [36] |
| $C_6H_5C(CH_3)_2$ | 0.026 | 0.007 | — | — | — | [33] |
| $C_6H_5CHCH_3$ | 0.024 | 0.006 | — | — | — | [33] |
| SH | 0.017 | 0.0089 | 22 | 2.8 | — | [36] |
| $C_6H_5CH_2$ | 0.015 | 0.004 | 51 | — | — | [33] |

Table 2 (cont'd.).

| X | $k \cdot 10^9$ | $f$ | $-Q_{XY}$ | $\Delta E$ | $E_{XY}$ | Refs. |
|---|---|---|---|---|---|---|
| Cl | ~0.006 | ~0.003 | 0 | — | — | [39] |
| $C_3$ | ⩽0.005 | ⩽0.002 | 37 | ⩾3.8 | — | [36] |
| $S_2$ | ⩽0.001 | ⩽0.0006 | 1 | ⩾4.4 | — | [36] |
| CN | ⩽0.001 | ⩽0.0005 | 27 | — | — | [39] |
| CN | ⩽0.0004 | ⩽0.0002 | 36 | ⩾5.0 | — | [36] |
| $NO_2$ | ⩽0.001 | ⩽0.00059 | 7 | ⩾4.4 | — | [36] |
| | | | Y=Br | | | |
| H | 3.7 | 0.43 | 95 | 0.50 | — | [36] |
| OH | 1.9 | 0.84 | 56 | — | — | [39] |
| OH | 0.99 | 0.43 | 57 | 0.50 | — | [36] |
| C | 1.3 | 0.48 | 64 | 0.43 | — | [36] |
| $CH_3NH$ | 1.3 | 0.72 | 82 | 0.19 | — | [36] |
| O | 1.1 | 0.48 | 66 | — | — | [36] |
| $NH_2$ | 1.1 | 0.48 | 71 | 0.43 | — | [36] |
| $CH_3O$ | 0.72 | 0.40 | 48 | — | — | [39] |
| $CH_3O$ | 0.73 | 0.40 | 49 | —(3.9—8.6) | 6.1—1.4 | [41] |
| $CH_3O$ | 1.1 | 0.61 | 62 | 0.29 | — | [36] |
| | | | Y=Br | | | |
| F | 0.60 | 0.28 | 37 | — | — | [39] |
| F | 1.2 | 0.59 | 39 | 0.31 | — | [36] |
| S | 0.46 | 0.26 | 31 | 0.80 | — | [36] |
| $CH_2Br$ | 0.42 | 0.32 | — | — | — | [36] |
| t-$C_4H_9$ | 0.41 | 0.30 | 43 | —(4.0—6.8) | 6.0—3.2 | [41] |
| HCC | 0.31 | 0.16 | 59 | —(2.2—7.0) | 7.8—3.0 | [41] |
| HCC | 0.52 | 0.26 | 73 | 0.80 | — | [36] |
| SH | 0.30 | 0.18 | 29 | 1.0 | — | [36] |
| $CH_2CN$ | 0.29 | 0.18 | 55 | — | — | [41] |
| $CH_2C(O)CH_3$ | 0.18 | 0.12 | 25 | — | — | [41] |
| $CH_3S$ | 0.14 | 0.091 | 39 | — | — | [39] |
| $CH_3S$ | 0.52 | 0.35 | 43 | 0.62 | — | [36] |
| $S_2$ | 0.033 | 0.024 | 8 | 2.2 | — | [36] |
| $C_2$ | 0.032 | 0.016 | 44 | 2.5 | — | [36] |
| CN | 0.02 | 0.01 | 35 | — | — | [39] |
| CN | 0.03 | 0.016 | 43 | 2.4 | — | [36] |
| $CH_3COO$ | 0.020 | 0.014 | 17 | —(2.6—6.1) | 7.4—3.9 | [41] |
| PhN | 0.019 | 0.015 | 48 | — | — | [41] |
| Cl | 0.012 | 0.0070 | 8 | — | — | [39] |
| Cl | 0.021 | 0.012 | 7 | 2.6 | — | [36] |
| Br | <0.01 | <0.008 | 0 | — | — | [39] |
| $NO_2$ | ⩽0.001 | ⩽0.0006 | 14 | ⩾4.4 | — | [36] |
| | | | Y=$CF_3COO$ | | | |
| OH | 1.4 | 0.47 | 68 | — | — | [39] |
| F | 1.1 | 0.39 | 49 | — | — | [39] |
| $CH_3O$ | 1.0 | 0.43 | 60 | — | — | [39] |
| $CH_3S$ | 0.50 | 0.25 | 52 | — | — | [39] |
| Cl | 0.045 | 0.021 | 21 | — | — | [39] |
| CN | 0.03 | 0.01 | 48 | — | — | [39] |
| Br | ~0.005 | ~0.003 | 13 | — | — | [39] |
| | | | Y=$C_6H_5O$ | | | |
| OH | 0.08 | 0.03 | 38 | — | — | [39] |
| F | 0.08 | 0.03 | 19 | — | — | [39] |
| $CH_3O$ | 0.024 | 0.012 | 30 | — | — | [39] |
| CN | ~0.007 | ~0.003 | 18 | — | — | [39] |
| $CH_3S$ | <0.005 | <0.003 | 22 | — | — | [39] |
| | | | Y=$CH_3O$ | | | |
| $CD_3O$ | <0.001 | <0.0005 | 0 | — | — | [39] |
| | | | Y=SH | | | |
| $CH_3S$ | 0.8 | 0.5 | 12 | — | — | [39] |

Remarks. The measurements of Bohme and Young[33] and Tanaka et al.[36] were made by the method of afterglow in a stream and the $\Delta E$ were estimated from the Arrhenius equation with the pre-exponential factor equal to the collision frequency; Pellerite and co-workers[39,41] carried out their measurements by the ICR method, $\Delta E$ was estimated by the RRKM method, and $E_{XY}$ was calculated on the assumption that the formation energy of the complex is −9 kcal $mol^{-1}$.

The efficiency $f = k/k_c$ is defined as the ratio of the observed rate constant $k$ to the gas-phase kinetic rate of collision $k_c$. The range of the gas-phase ion–molecule reaction rates is usually small. For example, the proton transfer reactions in systems with a localised charge are rapid and $f \cong 1$ for such processes. The low efficiency and the long range of its variation indicate an unusual character of the reactions quoted in Table 2.

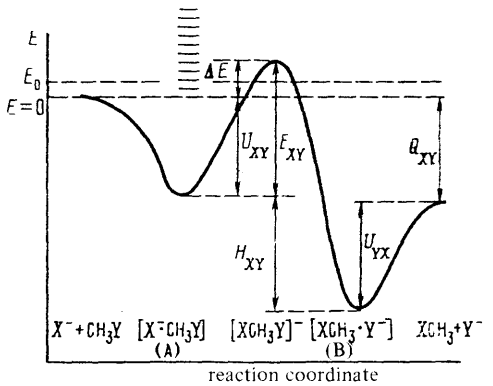



**Figure 4.** The PES profile for a gas-phase reaction of the $S_N2$ type; $E_0$ is the kinetic energy of the reactants and the short horizontal lines represent schematically the energy levels of the "hot" prereaction complex located above the intrinsic energy of the reactants ($E = 0$).

A model kinetic description of a multistage exothermic process with a two-well potential profile has been proposed by Brauman and co-workers[39–41] and is based on the scheme

$$X^- + CH_3Y \underset{k_1}{\overset{k_0}{\rightleftarrows}} [X^- \cdot CH_3Y] \qquad (6)$$

$$[X^- \cdot CH_3Y] \xrightarrow{k_2} \text{products} \qquad (7)$$

to which correspond simple expressions for the observed rate constant and efficiency:

$$k = k_0 k_2/(k_1 + k_2) \ , \qquad f = (1 + k_1/k_2)^{-1} \ . \qquad (8)$$

The relation $k_1/k_2 \gg 1$ corresponds to the data in Table 2. This inequality may be ensured even for negative $\Delta E$ with a not unduly large absolute value (the barrier for the process with $k_2$ is lower than the barrier for the process with $k_1$), because the large distance between the reactants in the TS of the reverse reaction (6) increases the freedom of their relative movement.

The simplest estimate of the $k_1/k_2$ ratio within the framework of the activated complex theory is

$$k_1/k_2 = (A_1/A_2)\exp(\Delta E/RT) \ . \qquad (9)$$

The pre-exponential factors $A_1$ and $A_2$ are calculated by standard methods. Eqn.(9) is valid if the distribution function for the complexes $[X^-.CH_3Y]$ corresponds to equilibrium, i.e. if the rate of deactivation (as a result of collisions) of the "hot" complexes formed via reaction (6) is much higher than the rate of their decomposition defined by the constants $k_1 + k_2$. Experiments[39–41] carried out at a low pressure ($10^{-5}$–$10^{-6}$ mmHg) do not satisfy this relation. The statistical unimolecular decomposition theory (RRKM) was used to estimate $k_1/k_2$ under such conditions. It was assumed that the "hot" complex formed decomposes via one of the possible pathways, without undergoing even a single collision, and that its energy $E = E_0 + U_{XY} = E_0 + E_{XY} - \Delta E$ (Fig.4) is distributed statistically among the internal degrees of freedom. The following approximate expression is valid within the framework of this model:[39]

$$\frac{k_1}{k_2} \cong \frac{\int_{U_{XY}}^{\infty} G_1(E - U_{XY}) \exp(-E/kT)\, dE}{\int_{U_{XY}}^{\infty} G_2(E - E_{XY} - \Delta E_{rot}) \exp(-E/kT)\, dE} \ , \qquad (10)$$

where $G_1(E)$ and $G_2(E)$, i.e. the numbers of the vibrational-rotational states in a microcanonical ensemble with the energy $E$ for the corresponding activated complexes, were calculated by the RRKM method (the energy arguments are indicated in brackets; $\Delta E_{rot}$ is the adiabatic change in the rotational energy in the TS). The independent experimental estimate $U = -9$ kcal mol$^{-1}$ was adopted for the energy of formation of the complexes $U_{XY}$, after which only one unknown parameter remains in Eqn.(10)—the height of the internal barrier $E_{XY}$; this quantity was chosen in such a way that the experimental efficiencies were consistent with Eqn.(8).

Unfortunately the results obtained are not unambiguous because of the arbitrary choice of the activated complex models in the calculation of $G_1$ and $G_2$ (see the scatter of the estimates of $\Delta E$ and $E_{XY}$ in Table 2). In order to refine the model, more detailed experimental information is essential.

A temperature variation of the rate constant $k$ has been investigated[42] in the range 25–390 °C for the reactions

$$Cl^- + RBr \rightarrow ClR + Br^-$$
$$R = CH_3,\ C_2H_5,\ \text{iso-}C_3H_7,\ \text{n-}C_4H_9,\ \text{iso-}C_4H_9.$$

The ratio $k_1/k_2$ was estimated using the activated complex theory [Eqn.(9)] on the grounds that the experiment was performed at a fairly high pressure (~4 mmHg). The estimates of their height proved to be much less ambiguous:

| R | $CH_3$ | $C_2H_5$ | n-$C_4H_9$ | iso-$C_3H_7$ | iso-$C_4H_9$ |
|---|---|---|---|---|---|
| $E_a$, kcal mol$^{-1}$ | −2.5 | 0.8 | −0.5 | 5.1 | 5.7 |

According to Eqn.(9), negative values of $\Delta E$ should lead to a negative observed activation energy $E_a$, which in a rough estimate agrees with $\Delta E$ as regards absolute magnitude (in an exact calculation account is taken of the temperature variation of the pre-exponential factors). The negative value $E_a \cong -2$ kcal mol$^{-1}$ has indeed been observed in the reaction with the $CH_3Br$ substrate.

The validity of such treatment of kinetic experiments is far from evident. In a non-equilibrium situation the very kinetic scheme defined by Eqns.(6) and (7), which ignores the direct mechanism involving the collision of the species, unassociated with the formation of the pre-reaction complex, is doubtful. If an appreciable fraction of the reaction product is formed via the direct mechanism, Eqn.(8) has no significance. Quantum-dynamic calculations have shown[43,44] that the contribution of the direct process to the formation of products is different in different systems. For thermally neutral and endothermic reactions ($Q_{XY} \geq 0$), it is appreciable. On the other hand, for exothermic reactions ($Q_{XY} < 0$), the direct mechanism leads to almost complete reflection (the probability of reflection in the direct process, amounting to 0.998 for $\Delta E = -1.9$ kcal mol$^{-1}$, has been found for $H^- + CH_3F$) and its contribution to the reaction may be neglected. In this case the reaction does indeed proceed

via the formation of the complex $[X^-.CH_3Y]$ and it would be incorrect to calculate the efficiency $f$ by Eqns.(8) and (10). The low efficiency is associated with the low probability of the formation of the complex. It can be calculated from the formula:[45]

$$f = (h/kT)\sum_{\lambda} P_{0\lambda}k_{2\lambda}\exp(-E_\lambda/kT),$$

where $h$ is the Planck constant, $P_{0\lambda}$ the probability of the formation of the "hot" complex in the vibrational state $\lambda$ with the energy $E_\lambda$ (reckoned from the energy of the reactants $E = 0$—see Fig.4), and $k_{2\lambda}$ the rate constant for the decomposition of this state to the products. The quantities $P_{0\lambda}$ and $k_{2\lambda}$ are found in the dynamic calculation.

Table 3. Results of the calculations of the parameters of the complexes or TS of the type $[XCH_3Y]^-$ by various methods.

| Bond lengths, Å | | $\Delta E$, kcal mol$^{-1}$ | Method (basis set) | Refs. |
|---|---|---|---|---|
| X—C | C—Y | | | |
| | | $[HCH_3H]^-$ | | |
| 1.225 | 1.225 | —13.3[a] | MINDO/3 | [70] |
| 1.189 | 1.189 | —26.1[a] | CNDO/BW | [72] |
| 1.250 | 1.250 | —2.4[a] | MNDO | *b* |
| 1.481 | 1.481 | 46.0 | STO-3G | [14] |
| 1.702 | 1.702 | | 3-21G | [14] |
| 1.730 | 1.730 | 48.8 | 4-31G | [14] |
| 1.715 | 1.715 | | 6-311G* | [14] |
| 1.736 | 1.736 | 51.7 | (10 6/5) → [5 4/3] | [52] |
| — | — | 46.2 | *c* | [52] |
| — | — | 51.2 | *d* | [52] |
| — | — | 47.2 | *e* | [52] |
| 1.736 | 1.736 | 63.6 | (8.4/4) → [4 2/2] | [53] |
| | | 56.4 | *f* | [53] |
| 2.00 | 2.00 | 48.0 | semiemp. | [72] |
| | | $[HCH_2F]^-$ | | |
| — | — | —57.3[a] | MINDO/3 | [70] |
| 2.41 | 1.88 | 16.7 | semiemp. | [72] |
| 1.924 | 1.726 | —12.4 | 4-31G | [14] |
| 1.937 | 1.958 | 12 | (8.4/4) → [4.2/2] | [53] |
| — | — | 10 | *f* | [53] |
| 1.937 | 1.958 | 3.8 | (11.7/6 → [5.3/3]) | [32] |
| | | $[FCH_2F]^-$ | | |
| 1.45 | 1.45 | —88.3[a] | CNDO/2 | [74, 69] |
| — | — | —33.4[a] | STO-3G | [12] |
| 1.643 | 1.643 | 40 | MNDO | *b* |
| 1.828 | 1.828 | —14.6 | 4-31G | [12] |
| 1.878 | 1.878 | —8.8 | (9.5/4) → [5.3/3] | [46] |
| — | — | —3.3 | (9,5/4) → [5,3/3] + diffuse AO | [49] |
| 1.94 | 1.94 | 5.2 | semiemp. | [72] |
| — | — | —2.2 | 6-311G* | [14] |
| 1.878 | 1.878 | 7.9 | (11.7/6 → [5.3/3] | [32] |
| 1.823 | 1.823 | 0.2 | (10 6/5) → [5.4/3] | [52] |
| — | — | 2.1 | *c* | [52] |
| 1.805 | 1.805 | 4.2 | (8.4/4) → [4.2/2] | [53] |
| — | — | 8.9 | *f* | [53] |
| | | $[ClCH_2Cl]^-$ | | |
| 2.150 | 2.150 | 4.4 | MNDO | [73] |
| — | — | —10 | 3-21G | [62] |
| 2.382 | 2.382 | —10.9 | 4-31G | [14] |
| — | — | 3.6 | 6-311G* | [75] |
| 2.391 | 2.391 | 2.2 | (8.4/4) → [4.2/2] | [53] |
| — | — | 9.7 | *f* | [53] |

[a]Complex, there is no saddle point on the PES; all the remaining configurations correspond to saddle points on the PES.

[b]Our results.

[c,d,e]The calculation was performed with addition of polarisation and diffuse functions to the (10,6/5) → [5,4/3] minimal basis set, namely: [c]$d$(C) and $p$(H); [d]$d$(C); [e]$p$(H).

[f]The configuration interaction was taken into account by the CEPA-PNO method in terms of the minimal basis set (8,4/4) → [4,2/2].

Thus the low efficiency of the non-activated ($\Delta E < 0$) reactions under non-equilibrium conditions (low pressure) can be accounted for solely within the framework of a dynamic calculation. It is caused by the marked energy exchange between the reaction coordinate and the transverse vibrational degrees of freedom in the region of the free reaction complex.

## 3. Calculations of the Potential Energy Surfaces

Reactions (5) of the $S_N2$ type at a saturated carbon atom have been investigated vigorously by quantum-chemical methods—mainly non-empirical methods[11-14,32,46-66] and more rarely by semiempirical methods.[1,7,10,15,16,67-73] The complex two-well profile of the potential curves is reproduced satisfactorily only in calculations at a sufficiently high level. Practice has demonstrated that semiempirical methods are as a rule unsuitable for the calculation of the PES for such reactions; this is illustrated in Table 3. Their application has therefore been restricted to the study of qualitative relations (the study of stereochemistry or of the effect of substituents). Methods using the approximation involving the neglect of differential overlap (NDO) yield a qualitatively incorrect potential surface for reaction (5), predicting the formation of a stable pentacoordinate complex (the presence of a minimum on the PES), for example $CH_5^-$ or $CH_3F_2^-$, instead of the saddle point.[67,70] The geometry of these complexes differs considerably from the geometry of the TS calculated by non-empirical methods: the axial bonds in the complex are shorter by ~0.5 Å than in the TS.

The stability of the structures $[XCH_3Y]^-$ is found to be too high in calculations by semiempirical methods for two reasons. Firstly, the form of the valence atomic orbitals of X and Y changes appreciably and their atomic charges are altered in the course of the reaction, which is characteristic of anionic reactions where X and Y are isolated atoms, particularly when X = Y = H. If X and Y are molecular residues, then the errors diminish because of the delocalisation of the excess electron densities.

Secondly, the NDO approximation introduces a significant error. The empirical inclusion of non-orthogonality effects in the parameters of the semiempirical methods is intended for neutral molecules and cations (included in the calibration set in the optimisation of the parameters of the MINDO and MNDO methods). As a result, one of the components of the total energy, namely the contribution of the exchange repulsion, is underestimated if the excess electron populations on the atoms of the reaction centre are large. In calculations for cationic systems, the latter defect is removed. This is confirmed by the result, likely to be correct, obtained in calculations for cationic reactions by the MINDO/3 [71] and MNDO [16] methods. The potential curves for $S_N2$ reactions with neutral nucleophiles, $\ddot{X} + RN_2^+ \rightarrow XR^+ + N_2$ (R = $CH_3$ or $C_2H_5$), calculated by the MNDO method, have a characteristic two-well profile with minima 3–10 kcal mol$^{-1}$ deep and separated by a barrier. However, the parametrisation of the MNDO method successfully models the exchange repulsion also in certain anionic systems. For example, two-well potential curves have been obtained for the following anionic $S_N2$ reactions: $CN^- + CH_3CN$,[6] $Cl^- + RCl$ (R = alkyl or $R'C_6H_4CH_2$), and $X^- + CH_3Cl$ (X = Cl, HO, HS, $CH_3O$, $CH_3S$, $H_2N$, CN, NC, or HCC).[73] The best result was obtained for X = Cl (Table 3). This is because the calibration of the parameters of the Cl atom in the MNDO method reproduces its electron affinity, i.e. is in fact designed for the description of the $Cl^-$ anion. For the majority of other anions with the charge localised on one

atom, the errors in the heats of formation are now as much as 20–30 kcal mol$^{-1}$ and this affects the calculated energy parameters of the reactions.[73] Calculations with the aid of MNDO, as well as other NDO methods, for the $H^- + CH_4$ reaction yield a false minimum for the symmetrical configuration and the barrier of the $F^- + CH_3F$ reaction is unacceptably high (Table 3).

The semiempirical method based on the explicit allowance for the AO non-orthogonality effects[76,77] has been used successfully in the calculations on the kinetics of a series of $S_N2$ reactions. In this method the integrals are parametrised in terms of an atomic basis set and are then converted to an orthogonal basis set. This procedure eliminates the disadvantages of the NDO approximation and the method yields characteristic two-well curves for reactions (5) with X, Y = H, F, Cl, or OH.[72]

The effect involving a change in the form of the AO following a change in the atomic charges, indicated above, cannot be taken into account in non-empirical methods employing a minimal basis set either. It can be estimated by comparing the results of calculations in terms of the STO-3G basis set and in terms of an extended basis set (Table 3). The axial bonds in a TS of the type of $CH_5^-$ found in terms of the limited STO-3G basis set are too short. A more significant feature is that the forms of the potential curve for the $F^- + CH_3F$ reaction correspond to the formation of a stable complex instead of the TS, as in semiempirical methods.

The electronic correlation contribution in calculations on reactions (5) is weak (Table 3) and, according to the available calculations,[53,66] does not introduce significant changes into the barrier on the PES.

A series of studies[14,32,53,58,59,72] have been devoted to systematic calculations of the PES for reactions (5), including the TS and complexes. The results of the best calculations are presented in Table 4. The majority of the PES have been calculated in terms of the moderate 4-31G basis set with two exponential functions with respect to the valence shell. Table 3 illustrates the effect of the basis set. A reliable geometry of the stationary points is usually obtained at the level of the 4-31G basis set. However, in order to obtain reliable energy parameters, a wider basis set is required. Thus the energies of the TS in the $F^- + CH_3F$, $Cl^- + CH_3Cl$, and $H^- + CH_3F$ systems, calculated in terms of the 4-31G basis set[12,14] and by the CEPA-PNO method {balanced basis set (8,4/4) contracted to [4,2/2] taking into account electron correlation}[53] differ by 20 to 25 kcal mol$^{-1}$ and have opposite signs relative to the energies of the reactants. A saddle point is not obtained in the PES for the $H^- + CH_3Cl$ [56] and $F^- + CH_3Cl$ [14] reactions in the 4-31G method, which conflicts with the calculations in terms of a wider basis set.

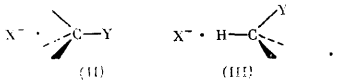
Two minima on the potential energy profile correspond to electrostatic ion–molecule complexes. The calculated characteristics of the complexes agree with the experimental data. Their calculated energy of formation is in most cases between −10 and −20 kcal mol$^{-1}$. The complexes are highly asymmetric. When X = Y, the length of one bond (X.C) is more than 2.5 Å, while that of the other (C–X) is close to the equilibrium value in the substrate. The calculated length of the X.C bond sometimes depends significantly on the basis set of the computational method. In [$H^-$.$CH_3F$] the length of the H.C bond, calculated in terms of the 4-31G basis set, is 2.64 Å, whilst that calculated in terms of 6.311G*

Table 4. The geometrical and energy characteristics of the PES for the reactions $X^- + CH_3Y \rightarrow XCH_3 + Y^-$ (bond length, Å; energy, kcal mol$^{-1}$).

| No. | X | Y | Complex (A) | | | Transition state | | | | Complex (B) | | | $Q_{XY}$ | Method (basis set) | Refs. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | X·C | C–Y | $U_{XY}$ | X–C | C–Y | $E_{XY}$ | $\Delta E$ | X–C | C·Y | $U_{YX}$ | | | |
| 1 | H | H | — | — | — | 1.736 | 1.736 | — | 56.4 | — | — | — | 0 | (8.4/4)→[4.2/2] + Cl | [53] |
| 2 | F | F | — | — | — | 1.805 | 1.805 | — | 8.9 | — | — | — | 0 | ditto | [53] |
| 3 | HCC | CCH | 3.253 | 1.465 | −8.8 | 2.124 | 2.124 | 50.4 | 41.6 | — | — | — | 0 | 4-31 G | [14] |
| 4 | NC | CN | 3.086 | 1.459 | −14.9 | 2.112 | 2.112 | 43.8 | 28.9 | — | — | — | 0 | ditto | [14] |
| 5 | $N\bar{H}_2$ | $\bar{N}H_2$ | — | — | −10.0 | 2.002 | 2.002 | 37.7 | 27.7 | — | — | — | 0 | » | [14] |
| 6 | $C\bar{N}$ | $\bar{N}C$ | 2.902 | 1.441 | −14.6 | 2.013 | 2.013 | 28.5 | 13.9 | — | — | — | 0 | » | [14] |
| 7 | $C\bar{H}_3O$ | $\bar{O}CH_3$ | 2.876 | 1.450 | −11.5 | 1.898 | 1.898 | 23.5 | 12.0 | — | — | — | 0 | » | [14] |
| 8 | HS | $\bar{S}H$ | 3.442 | 1.914 | −9.9 | 2.450 | 2.450 | 15.5 | 5.6 | — | — | — | 0 | » | [14] |
| 9 | HO | OH | 2.807 | 1.463 | −15.7 | 1.908 | 1.908 | 21.2 | 5.5 | — | — | — | 0 | » | [14] |
| 10 | HOO | OOH | — | — | −13.2 | 1.920 | 1.920 | 18.7 | 5.3 | — | — | — | 0 | » | [14] |
| 11 | FO | OF | 2.962 | 1.468 | −22.0 | 1.932 | 1.932 | 18.8 | −3.2 | — | — | — | 0 | » | [14] |
| 12 | Cl | Cl | — | — | — | 2.391 | 2.391 | — | 9.7 | — | — | — | | (8.4/4)→[4 2/2] + Cl | [53] |
| 13 | H | OH | 2.875 | 1.461 | −13.0 | 1.838 | 1.844 | 18.5 | 5.5 | — | — | −60.6[a] | −47.4 | 4-31 G | [14] |
| 14 | H | CCH | 2.966 | 1.468 | −11.7 | 1.886 | 1.991 | 34.9 | 23.2 | — | — | −54.1[a] | −48.2 | 4-31 G | [14] |
| 15 | H | F | — | — | — | 1.937 | 1.958 | — | 10 | — | — | — | −53.8 | (8.4/4)→[4.2/2] + Cl | [53] |
| 16 | H | Cl | — | — | — | 2.117 | 2.122 | — | −6.8 | — | — | — | −86.7 | ditto | [53] |
| 17 | H | CN | 2.829 | 1.463 | −20.4 | 1.964 | 1.923 | 23.6 | 3.2 | — | — | −83.8[a] | −78.2 | 4-31 G | [14] |
| 18 | H | $\bar{N}H_2$ | — | — | — | 1.764 | 1.981 | — | 27.4 | — | — | −34.0[a] | −23.5 | ditto | [14] |
| 19 | H | $\bar{N}C$ | 2.752 | 1.453 | −20.6 | 2.075 | 1.773 | 9.7 | −10.9 | — | — | −103.7[a] | −99.6 | » | [14] |
| 20 | $H_2N$ | $\bar{F}$ | — | — | — | 1.728 | 2.138 | — | −13.4 | — | — | — | −43.3 | » | [14] |
| 21 | $H_2N$ | CN | — | — | — | 2.169 | 1.933 | — | 3.1 | — | — | — | −94.7 | » | [14] |
| 22 | HO | $\bar{C}CH$ | — | — | — | 1.960 | 2.054 | — | 23.4 | — | — | — | −0.7 | » | [14] |
| 23 | HO | Cl | 2.28 | 1.86 | −29.0 | 2.03 | 2.06 | 2.3 | −26.7 | 1.45 | 3.29 | −5.7 | −46.9 | semiemp. | [72] |
| 24 | HO | F | 2.573 | 1.461 | −22.8 | 1.775 | 1.973 | 9.1 | −13.7 | 1.466 | 2.579 | −38.3 | −19.4 | 4-31 G | [14] |
| 25 | HO | CN | 2.742 | 1.456 | −24.5 | 2.018 | 1.966 | 27.0 | 2.5 | 1.451 | 3.158 | −39.6 | −30.8 | ditto | [14] |
| 26 | F | $\bar{C}N$ | 2.552 | 1.459 | −27.9 | 1.902 | 2.008 | 29.3 | 1.4 | 1.440 | 2.976 | −25.2 | −11.4 | » | [14] |
| 27 | F | $\bar{O}OH$ | 2.727 | 1.450 | −25.2 | 1.907 | 1.832 | 14.1 | −11.1 | 1.451 | 2.713 | −31.8 | −13.8 | » | [14] |
| 28 | F | NC | — | — | — | 1.973 | 1.899 | — | −15.2 | — | — | — | −32.7 | » | [14] |
| 29 | F | $\bar{O}F$ | — | — | — | 1.986 | 1.765 | — | −26.0 | — | — | — | −38.0 | 4-31 G | [14] |
| 30 | F | Cl | — | — | — | 2.178 | 2.072 | — | −15.7 | — | — | — | −45.0 | (8.4/4)→]4 2/2] + Cl | [53] |

[a]Complex of type (III).

basis set is 3.06 Å.[14] The bond in the complex can be formed in two ways, to which correspond two local minima on the PES:[12,14]



(II) (III)

For X = Y = F, the energy of complex (II) is lower by only 0.1 kcal mol$^{-1}$ than that of complex (III) and the barrier to the transformation (II) → (III) is 0.8 kcal mol$^{-1}$.[12] On the other hand, if the substrate is $CH_4$, then the complex of type (III) is more stable.

The configuration of the TS of reactions (5) corresponds to the apex of the internal barrier. The energy of the TS can be not only higher ($\Delta E > 0$) but also lower ($\Delta E < 0$) than those of reactants (Table 4 and Fig. 4). This has apparently been confirmed by experiment.[36,41,42]

The geometry and the changes in the X–C and C–Y distances in the TS compared with equilibrium X–C and C–Y bond lengths are listed in Table 5 for some reactions. The X–C and C–Y bonds in the TS are longer than the equilibrium bonds by 0.3–0.8 Å and differ greatly for a series of reactions based both on the nucleophile and on the leaving group.

Table 5. The geometry of the TS and the energy characteristics of reactions of type (5); the changes in the length of the axial bonds relative to the equilibrium values in the substrates $XCH_3$ and $CH_3Y$ (the bond lengths are in Å, the angles in degrees, and the energy in kcal mol$^{-1}$) (the calculation was performed in terms of the 4-31G basis set using Mitchell's data[14]).

| X | Y | $R$(X–C) | Δ(X–C) | $R$(C–Y) | Δ(C–Y) | α(H–C–Y) | $\Delta E$ | $H_{XY}$ | $Q_{XY}$ |
|---|---|---|---|---|---|---|---|---|---|
| H | F | 1.92 | 0.82 | 1.73 | 0.29 | 96.3 | −12.4 | −62.5 | −66.8 |
| $H_2N$ | F | 2.14 | — | 1.73 | 0.29 | 94.1 | −13.4 | — | −63.3 |
| HO | F | 1.97 | 0.42 | 1.78 | 0.34 | 93.2 | −13.7 | −15.5 | −49.4 |
| HCC | F | 2.11 | 0.64 | 1.84 | 0.40 | 90.3 | −5.0 | −21.3 | −48.7 |
| $CH_3O$ | F | 1.94 | 0.46 | 1.82 | 0.38 | 90–91.5 | −4.2 | — | −5.7 |
| H | CN | 1.96 | 0.86 | 1.92 | 0.48 | 97.5 | 3.2 | −63.4 | −78.2 |
| $H_2N$ | CN | 2.17 | — | 1.94 | 0.49 | 95–96.2 | 2.1 | — | −54.7 |
| HO | CN | 2.02 | 0.57 | 1.97 | 0.53 | 95–95.8 | 2.5 | −15.1 | −30.8 |
| F | CN | 1.96 | 0.46 | 2.01 | 0.57 | 92.8 | 1.4 | 2.7 | −11.4 |
| H | NC | 2.08 | 0.98 | 1.77 | 0.33 | 99.6 | −10.8 | −83.1 | −99.6 |
| H | CN | 1.96 | 0.86 | 1.92 | 0.48 | 97.5 | 3.2 | −63.4 | −78.2 |
| H | F | 1.92 | 0.82 | 1.73 | 0.29 | 95.3 | −12.4 | −62.5 | −66.8 |
| H | CCH | 1.86 | 0.79 | 2.00 | 0.54 | 95.1 | 23.2 | −42.4 | −48.2 |
| H | OH | 1.84 | 0.74 | 1.84 | 0.39 | 91.7 | 5.5 | −47.0 | −47.0 |
| H | $NH_2$ | 1.76 | 0.66 | 1.98 | — | 94.6 | 27.4 | — | −23.5 |
| H | H | 1.74 | 0.64 | 1.74 | 0.64 | 90 | 48.8 | 0 | 0 |
| F | OF | 1.99 | 0.55 | 1.77 | 0.33 | 93.3 | −26.0 | — | −38.0 |
| F | NC | 1.97 | 0.53 | 1.85 | 0.41 | 95.2 | −15.2 | — | −32.7 |
| F | $OC_2H_3$ | 1.94 | 0.50 | 1.82 | — | 91–97 | −12.0 | — | −22.9 |
| F | OOH | 1.91 | 0.47 | 1.83 | 0.38 | 90.2 | −11.4 | −6.6 | −13.8 |
| F | NC | 1.90 | 0.46 | 2.01 | 0.56 | 92.8 | 1.4 | 2.7 | −11.4 |

It was noted earlier[14,32,72] that Hammond's postulate holds in the $X_i$ + $CH_3Y$ reactions, which is illustrated in Table 5. This is a familiar, consistent relation between the structure of the TS and the heat of reaction, according to which the position of the TS shifts less along the reaction coordinate the higher the heat change $Q$. The change in the valence angle Δ(H–C–Y) or the increase in the bond length Δ(C–Y) in TS of the type $[XCH_3Y]^-$ compared with the equilibrium values in the substrate $CH_3Y$ can be adopted as measures of the above shift. Table 5 shows that both quantities are correlated with $Q$. This apparently exhausts the simple regularities in gas-phase reactions. The correlation usually postulated between the height of the activation barrier of the reaction $\Delta E$ and the heat of reaction $Q$ is not observed, in agreement with gas-phase experiments, if it is assumed that the measured reaction rate constant characterises the height of the barrier $\Delta E$ (Table 2).

The lack of simple correlations for gas-phase reactions of the $S_N2$ type can be accounted for by two causes. Firstly, for a complex two-well profile of the potential curve, the conditions essential for the derivation of the Bell–Evans–Polanyi principle or Hammond's postulate do not hold (they are considered in Appendix 2). From this standpoint, one is more justified in expecting a correlation between the geometry of the TS and the heat of the "complex → complex" stage, which is equal to $H$.

The estimation of reactivity-nucleophilicity, the mobility of the leaving group (nucleofugacity), etc. from calculated data is also difficult owing to the complex form of the PES. An uncertainty arises because it is not known which of the calculated quantities, $\Delta E$ or $E$, should be used as the measure of the reactivity. Furthermore, as stated in Section III.2, the kinetic models for the description of multistage $S_N2$ processes are not unambiguous and it is not clear whether the characteristics of the potential curve are susceptible to a simple kinetic interpretation.

Secondly the lack of simple relations is associated with the fact that the replacement of X or Y in the reaction centre XCY alters the structure of the TS too drastically. For example, this is manifested in the length of the axial bonds. Table 5 shows that the quantities Δ(C–Y) differ in the range 0.1–0.3 Å even in narrow series. Different TS actually correspond to series in which the nucleophile X or the leaving group Y are altered. This explains why the experimental nucleophilicity series (variation of X) depend on the leaving group Y and the nucleofugacity series (variation of Y) depend on the nucleophile X.[37,72]

### 4. Attempts at a Theoretical Study of Reactions in Solution. Problems Involving Allowance for the Medium

The gas-phase experiments and quantum-chemical calculations examined above refer to reactions of isolated chemical systems. However, $S_N2$ reactions in solution are of direct practical interest. They require special consideration, as can be seen from the following facts:

(1) The rates of typical $S_N2$ reactions decrease by 10–20 orders of magnitude on passing from the gas phase to a polar solvent[36,39,78] [the logarithm of the rate constant for the $F^-$ + $CH_3Cl$ reaction at 25 °C is 11.7 (litre mol$^{-1}$ s$^{-1}$) in the gas phase and −7.8 (litre mol$^{-1}$ s$^{-1}$) in water].

(2) The activity series of nucleophiles can be different in the gas phase and in solution and also vary as a function of the solvent (the gas-phase activity series $F^- > Cl^- > Br^- > I^-$ is inverted on passing to proton-donating media[79]).

(3) The solvent can alter the mechanism of an $S_N2$ reaction: in solution the latter can proceed via a preliminary stage involving the formation of ion pairs up to the change of the mechanism to the $S_N1$ type.

Such a marked influence of the solvent on the chemical process is specific to reactions with participation ions. Strong electrostatic (ion–dipole) interactions arise in these systems. They in fact determine the characteristic features of reactions in polar media. The intensity of the ion–dipole interactions is comparable to that of interactions responsible for the chemical reaction proper in an isolated system. Any theory, quantitative or qualitative, claiming to explain the kinetics of $S_N2$ reactions in solution cannot ignore the presence of the medium.

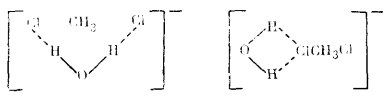
Attempts at experimental[33,80–83] and theoretical[62] study of the influence of the solvent have been undertaken in relation to $S_N2$ reactions with participation of a small number of solvating molecules. In gas-phase experiments with hydrated nucleophilic species,[80,81] i.e.

$$HO^- \cdot n\,H_2O + CH_3Br \begin{cases} \longrightarrow HOCH_3 + Br^- \cdot n\,H_2O\ , & (11) \\ \longrightarrow HOCH_3 + Br^- + n\,H_2O\ . & (12) \end{cases}$$

measurements were made of the rate constants (in $cm^3$ molecule$^{-1}$ $s^{-1}$) and the following values were obtained at 300 K: $10^{-9}$ ($n = 0$); $(6 \pm 2) \times 10^{-10}$ ($n = 1$); $(2 \pm 1) \times 10^{-12}$ ($n = 2$); $2 \times 10^{-13}$ ($n = 3$); in aqueous solution: $k = 2.3 \times 10^{-25}$ $cm^3$ molecule$^{-1}$ $s^{-1}$.[78] The processes follow pathway (12), which is preferred for thermodynamic reasons: when $n \geq 3$, reaction (11) becomes endothermic. Indeed, it has been found[81] that the ionic ratio in the reaction product $Br^-.H_2O/(Br^- + Br^-.H_2O) = 0.04–0.07$.

Mechanism (12) has also been confirmed by systematic study of the reaction $X^-.nS + CH_3Y \rightarrow XCH_3 + (n-m)Y^- + mS$ (Y = Cl or Br; X = OD, $CH_3O$, $C_2H_5O$, $CH_3COCH_2$, HCOO, or $CH_3COO$).[82] It is of interest to compare with these data the quantum-chemical calculation of the PES for the reaction $Cl^-.nH_2O + CH_3Cl \rightarrow ClCH_3 + Cl^-.nH_2O$ ($n = 0, 1, 2$) by a non-empirical method (3-21G basis set) with complete optimisation of the geometry.[62]

According to the calculation, the prereaction electrostatic complexes are formed also in the case of the solvated nucleophile. Solvation increases their energy and the height of the internal barrier $E$ (Fig.4). The relief of the PES with one and especially two water molecules becomes very much more complex: intermediate structures, corresponding to different mechanisms of the transfer of $H_2O$ molecules from the nucleophile to the leaving group, appear. Two TS with similar energies have been found for $n = 1$:



The first corresponds to the simultaneous occurrence of the chemical and solvation rearrangements, while in the second the solvation rearrangement follows the chemical rearrangement. For $n = 2$, the following consecutive mechanism is energetically preferable: transfer of $H_2O$—chemical rearrangement—transfer of $H_2O$:

$$(H_2O)_2 \cdot Cl^- + CH_3Cl \rightarrow H_2O \cdots Cl^- \cdot CH_3Cl \cdots H_2O \rightarrow$$
$$\rightarrow H_2O \cdots ClCH_3 \cdot Cl^- \cdots H_2O \rightarrow ClCH_3 + Cl^- \cdot (H_2O)_2\ .$$

Several alternative reaction pathways have been observed together with that indicated above. The simultaneous occurrence of the $H_2O$ transfer and of the chemical rearrangement is the least favourable pathway.

Both experiment and calculation demonstrate the importance of solvation effects. On the other hand, it is evident that systems with a small number of solvent molecules are not successful models of reactions in solution. Indeed, although the measured constants did decrease, they remained within the range of "gas-phase" values. The formation of a desolvated anion in the reaction products is a specifically gas-phase mechanism, which does not occur in solution. The complex mechanisms of the transfer of water molecules noted in the calculation also have hardly any bearing on the real mechanisms in solution, where a collective rearrangement of the solvation shell, involving simultaneously many solvent molecules, is most probable.

The necessity to take into account explicitly a large number of solvent molecules is the main problem of the modern theory of chemical reactions in polar media. Two methods for its solution are being developed.[84,85] The so-called supermolecular approach considers the chemical system and the molecules of the medium on an equal basis in a single quantum-chemical calculation of the PES. An example is provided by the calculation described above.[62] It is clear from its consideration that the "supermolecules" for which the calculation is made must be fairly large. An analogous calculation of the solvation energies of ions with model potentials (which is technically incomparably simpler than the calculation of the PES) requires an explicit consideration of at least three coordination spheres, i.e. several hundred solvent molecules. In order to obtain concordant quantitative results, it is essential to optimise their positions and orientations, which are self-consistently determined by the electric field of the entire assembly of species forming the supermolecule and not only by the field of the "parent" ion. If account is taken of the multiplicity of the energy minima and the corresponding multiplicity of the reaction mechanisms, which is inevitable in such an investigation (an indication of this can be seen even in the simplest example discussed), then one can imagine how great are the technical difficulties in the solution of the problem.

Recent calculations for the $Cl^- + CH_3Cl$ reaction in water[75,86] and in dimethylformamide (DMF) [87] have demonstrated the present possibilities of this branch of research. The potential gas-phase reaction profile was calculated by a non-empirical method in terms of the 6-31G basis set. The interaction of the chemical subsystem with solvent molecules was taken into account with the aid of empirical atom–atom potentials calibrated against preliminary non-empirical calculations for simple model systems. This made is possible to take into account 250 water molecules and 180 DMF molecules surrounding the chemical subsystem. The configuration of the solvation shell was optimised by the Monte Carlo method. As a result of the calculation, the minima on the PES, to which correspond the electrostatic complexes found, as usual, for the gas phase, disappeared for the reactions in solution. The observed heights of the potential barriers proved to be 26.3 kcal mol$^{-1}$ for the reaction in water and 19.3 kcal mol$^{-1}$ for the reaction in DMF. The corresponding experimental activation energies are 26.6 and 22.7 kcal mol$^{-1}$.

In the second approach, the medium is regarded as a dielectric continuum in which the chemical system is immersed. For elementary situations, the solvation energy $U$ can be determined from simple formulae. For example, for a spherical ion with a radius $r$ in a medium having a dielectric constant $\varepsilon$, it can be calculated from the Born formula

$$U = e^2(1 - 1/\varepsilon)/2r\ .$$

In order to describe the chemical reaction in the continuous model, it is necessary to calculate the energy of the electrostatic interaction of the chemical system (with a complex distribution of electric charges) with the dielectric medium. The calculation is based on the same principles which lead to the Born formula, but in this case a cumbersome computer computation is required.[88] Ideally the calculation should be self-consistent, i.e. it should take into account the converse effect of the potential of the medium on the structure of the chemical system and the distribution of the electric charge in the latter.[89,90] There exist serious difficulties both in the selection of the dielectric constant (it does not agree with the usual macroscopic value) and in the selection of the size of the cavity in which the reacting system is placed. The

existing methods for the estimation of the size of the cavity, for example from the polarisability,[91] are not unambiguous.

All the foregoing considerations are based on the assumption that the solvation effects can be described within the framework of the activated complex theory. Only in this case is it sufficient to consider the stationary configurations of the initial and transition states of the reacting species + medium system. This is by no means evident. The orientational movements of solvent molecules which optimise the energy may not keep up with the movement of the reacting molecule; non-equilibrium reaction conditions then obtain.[92,93] In the continuous model the effective dielectric constant of the non-equilibrium medium diminishes.

As a consequence of all these problems, the published calculations of the PES for ion–molecule reactions in a polar solvent are usually far from perfect. The frankly empirical approaches employed have been discussed, for example, in the review of Abronin et al.[84] For nucleophilic substitution reactions, the continuous model has been used in calculations for the $X^- + CH_3F$ reactions, where X = OH or CN.[91]

The most elementary approach links the solvation effect to the shift of the energies of the frontier MO. For $S_N2$ reactions, calculations by the STO-3G method showed[94] that the formation of clusters of nucleophilic anions with several water molecules reduces the energies of the HOMO of the nucleophile, the effect increasing in the sequence $I^- < Br^- < Cl^-$. According to perturbation theory, the decrease of the HOMO level of the nucleophile, which increases the difference between this energy and the energy of the LUMO of the substrate, reduces the reactivity of the $Cl^-$ ion to a greater extent than that of $Br^-$ ion and the latter to a greater extent than the reactivity of $I^-$. Hence it follows that the nucleophilicity series $Cl^- > Br^- > I^-$, characteristic of aprotic solvents and the gas phase, can be inverted in a protic solvent.

We shall now consider the main causes of the changes which the PES for gas-phase $S_N2$ reactions undergo in solution. One of them is well known and consists in the fact that the electric charge in the TS is delocalised and the corresponding solvation energy is much smaller than the solvation energy of the nucleophilic ion with a localised charge. The loss of solvation energy has been estimated in several semiempirical calculations for the $F^- + CH_3F$ reaction.[74,95,96] According to the calculation by the MINDO/3 method, it amounts to 31 kcal mol$^{-1}$.[96] Calculation by the CNDO/2 method leads to clearly high values, which vary in the range 62–100 kcal mol$^{-1}$ as a function of the number of water molecules incorporated in the solvation shell.[74] A similar value (105 kcal mol$^{-1}$) has been obtained in the solvation model on the basis of the CNDO/2 method.[95] In the continuous model, the solvation energy differences calculated by the CNDO/2 method for the $X^- + CH_3F$ reaction[91] are 43 (X = OH) and 12.7 kcal mol$^{-1}$ (X = CN).

Although the semiempirical methods used are unsuitable for calculations on gas-phase reactions, the estimated solvation effect, which amounts to several tens of kcal mol$^{-1}$, is likely to be correct in terms of order of magnitude.

The second cause of the change in the form of the potential curve on passing from the gas phase to the solution becomes evident when the energies of the successive desolvation of ions are examined in relation to $F^-.nH_2O$: $\Delta H_{n,\,n-1}$ = −13.2 ($n$ = 5), −13.5 ($n$ = 4), −13.7 ($n$ = 3), −16.6 ($n$ = 2), and −23.3 kcal mol$^{-1}$ ($n$ = 1).[97] The reaction with the substrate is preceded by the formation of a contact ion–molecule pair with partial desolvation of the ion and the substrate in accordance with the idealised scheme

$$X^-\cdot nS + CH_3Y\cdot mS \rightleftarrows [X^-\cdot CH_3Y][(n+m-2)S] + 2S, \qquad (13)$$

where S is a solvent molecule. At this stage the amount of energy expended is approximately equal to the energy of the removal of one $H_2O$ molecule from the complete hydration shell of the nucleophilic ion. Together with the remaining solvation effects, it amounts to ~20 kcal mol$^{-1}$ for $F^-$. This is sufficient to understand why the formation of the electrostatic complexes is not observed in a polar solvent: the energy of their formation in the gas phase is as a rule less than the positive heat of reaction (13). The potential curves for the next, chemical stage proper, i.e.

$$[X^-\cdot CH_3Y][(n+m-2)S] \rightarrow \text{products}, \qquad (14)$$

are smoothed out acquiring the usual profile illustrated in Fig. 5. The barriers indicated by dashed lines correspond to the preliminary reaction (13) in which the solvation shells of the reactant are rearranged. In stage (14) the solvent exerts its influence in the usual way—via the shifts of the energies of the initial and transition states.

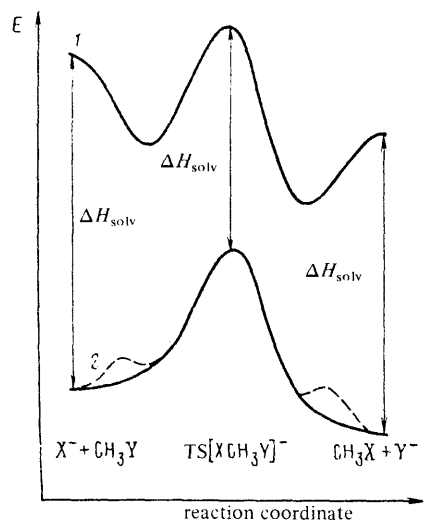



**Figure 5.** The change in the PES profile for an $S_N2$ reaction on passing from the gas phase (curve *1*) to a polar solvent (curve *2*). The dashed lines are explained in the text.

These considerations apply in the model calculation for reaction (14) with X, Y = F, Cl, or H.[98] The water molecules were replaced by point charges, forming dipoles. Their disposition and magnitudes were chosen so as to reduce the observed total solvation energies of the anions and the energies of their partial desolvation. In the calculation for reaction (14), one dipole each was removed from the solvation shell of the nucleophile and the substrate. In each external electric field specified in this way, the PES was calculated by a semiempirical method specially devised for calculations for the corresponding gas-phase reactions.[76,77]

The calculation reproduced the smooth potential profile for the reaction, because postulates designed to achieve this result were incorporated in the basis of the model of solvation shells adopted. The potential barrier found reflects the experimentally observed trends. It is of interest to compare the geometries of the TS found in solution and in

the gas phase for the $F^-$ + $CH_3Cl$ reaction, where these changes are most pronounced: $R(C-F)$ = 2.06 Å in solution and 2.14 Å in the gas phase and $R(C-Cl)$ = 2.35 Å and 2.24 Å in solution and in the gas phase respectively.

Thus, even if we confine ourselves to the description of the reactions in solution with the aid of the activated complex theory and the non-equilibrium character of the solvation effect is neglected, their standard treatment requires a significant revision. The calculation of the energy changes employing the "gas-phase" configurations of the reactants and of the activated complex is inadequate. It is necessary to take into account the distortion of the configuration of the PES in the region of the corresponding points under the influence of the medium. In the example considered, it has the character of a moderate correction in the case of the TS. However, in the region of the initial state the deformation of the PES is so great that one is justified in speaking of a change in the reaction mechanism.

### 5. The Effect of Substituents

The effect of substituents R both in the nucleophile $X(R^1)$ and in the substrate $C(R^2)-Y$ or $C-Y(R^3)$ on the reactivity can be naturally accounted for within the framework of a three-centre four-electron model of the open-chain TS:

$$\underset{\alpha_x}{[X(R^1)} \overset{\beta_{cx}}{---} \underset{\alpha_c}{C(R^2)} \overset{\beta_{cy}}{---} \underset{\alpha_y}{Y(R^3)]^-} \quad ;$$

(IV) (TS)

$$\underset{\alpha_x}{X^-(R^1)} + \underset{\alpha_c}{C(R^2)} \overset{\beta_0}{---} \underset{\alpha_y}{Y(R^3)} \quad \text{(initial state).}$$

(V)

The corresponding Coulombic ($\alpha$) and resonance ($\beta$) integrals are indicated in Schemes (IV) and (V) (the Hückel method).

It was noted above that the variation of the atoms X and Y alters the structure of the reaction centre so much that simple correlations are lacking in the corresponding reaction series. The introduction of substituents R for fixed X and Y makes it possible to construct narrow reaction series in which systematic changes in reactivity are observed.

The corresponding kinetic measurements have been as a rule made in polar aprotic solvents, which makes it possible to to adopt the usual smooth PES profile for the reactions considered. Other aspects of the effect of the solvent are usually ignored in a qualitative treatment.

According to perturbation theory for the interaction ($\beta_{cx}/\beta_0 \ll 1$, although this condition is by no means evident), the interaction of the highest occupied AO (MO) of the nucleophile $|x\rangle$ having the energy $\alpha_x$ with the LUMO of the substrate $|\sigma^*\rangle$ having the energy $\varepsilon_\sigma$ makes the main contribution to the change in the height of the potential barrier. Attempts have sometimes been made to explain the influence of the substituent by its effect on the energies of the corresponding frontier MO (i.e. on $\alpha_x$ or $\varepsilon_\sigma$). According to the Hückel MO theory, the interaction should alter $\alpha_x$ (for the substituent $R^1$ in the nucleophile) or $\varepsilon_\sigma$ (for substituents in the substrate) to a greater or lesser extent depending on the nature of the substituent. The interaction with electron-donating substituents (heteroatom with an electron pair) in the $\alpha$-position induces the greatest effect. It is to be expected that the introduction of such substituents into the nucleophile should increase the relative reactivity (the $\alpha$-effect), while their introduction into the substrate should diminish it. This model presupposes a purely resonance interaction of the substituent with the reaction centre.

The above treatment presupposes, in particular, that the levels of the substituent MO always lie below the level of the nucleophile HOMO. This is not always so and cases are known where direct calculation does not confirm the increase of the HOMO energy level predicted by the Hückel MO theory.[99] The effect is extremely sensitive to the spatial orientation of the substituent or more precisely of its unshared electron pair. This has been demonstrated by a non-empirical calculation of potential barriers for the $H^- + CH_3R \rightarrow CH_3R + H^-$ reactions, where R = OH, $NH_2$, or $BH_2$.[100]

We shall consider a reaction series with variation of a nucleophile of the type $X(R^1)$. In schemes (IV) and (V) it is characterised by the two variable parameters $\alpha_x$ and $\beta_{cx}$. For the standard system with $X(R_0^1)$, we shall designate them by $\alpha_x^0$ and $\beta_{cx}^0$. The energy of system (IV) relative to the standard system is then given by the following expression according to the perturbation theory:

$$\Delta E = E - E_0 = q_x^0(\alpha_x - \alpha_x^0) + 2P_{cx}^0(\beta_{cx} - \beta_{cx}^0) \ , \qquad (15)$$

where $q_x^0$ is the electronic charge on X and $P_{cx}^0$ is the order of the C–X bond in the TS of the standard system. If account is taken of the fact that $\alpha$ is a measure of the effective electronegativity of the atom X and $\beta$ is a measure of the effective capacity for the formation of a bond, then Eqn.(15) can be regarded as an analogue of the two-parameter empirical Edwards or Todesco–Bartoli equation[101,102] [in order to complete the derivation, it is necessary to formulate the analogous equation for the initial state (V) and subtract it from Eqn.(15)].

Suppose that only the substituents $R^1$ at X are varied. One can then fix $\beta_{cx} = \beta_{cx}^0$, which yields a one-parameter equation of the Hammett type. As will be shown below, it is then not essential to apply perturbation theory and $\alpha_x$ can be varied within wide limits.

The variation of the substituents $R^2$ at C or $R^3$ at Y can be treated in the same way by varying the corresponding Coulombic parameters $\alpha_c$ or $\alpha_y$. This corresponds to the induction model of the effect of substituents on reactivity which is an alternative to the resonance model mentioned above.

We shall designate the electronic energies of systems (IV) and (V) by $E(\alpha_i)$ and $E^0(\alpha_i)$ respectively ($i = x, c, y$). Suppose that $q_i$ and $q_i^0$ are the corresponding electronic charges in systems (IV) and (V). Since $q_i = \partial E/\partial\alpha_i$,[103] we have

$$E(\alpha_i + \Delta\alpha) = E(\alpha_i) + \int_{\alpha_i}^{\alpha_i+\Delta\alpha} q_i \, d\alpha \ ;$$

$$E^0(\alpha_i + \Delta\alpha) = E^0(\alpha_i) + \int_{\alpha_i}^{\alpha_i+\Delta\alpha} q_i^0 \, d\alpha \ .$$

The reactivity is determined by the quantity

$$\Delta_i = \Delta(\alpha_i + \Delta\alpha) - \Delta(\alpha_i) = [E(\alpha_i + \Delta\alpha) - E^0(\alpha_i + \Delta\alpha)] - [E(\alpha_i) - E^0(\alpha_i)] .$$

We thus obtain the expression

$$\Delta_i = \int_{\alpha_i}^{\alpha_i+\Delta\alpha} (q_i - q_i^0) \, d\alpha \ . \qquad (16)$$

If $q_i$ and $q_i^0$ change only slightly, the result obtained agrees with the conclusion reached from perturbation theory:

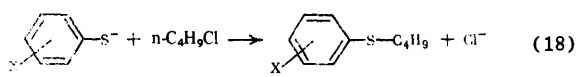
$$\Delta_i \cong (q_i - q_i^0)\Delta\alpha \ . \qquad (17)$$

When $\alpha_i$ changes by $\Delta\alpha$, the system becomes more or less reactive depending on whether the relative stabilisation energy $\Delta_i$ is positive or negative. Consequently analysis of

reactivity for a specified $\Delta\alpha$ reduces to the study of the sign of the difference $q_i - q_i^0$ in Eqn.(16) or (17). In the former case $q_i - q_i^0$ is assumed to be a variable-sign quantity.

The sign of $q_i - q_i^0$ for $\alpha_c \gg \alpha_x, \alpha_y$ is examined in Appendix 1. The results of the analysis are used below.

(1) Substituent in the nucleophile: $q_x - q_x^0 < 0$. The reactivity of the nucleophile (the nucleophilicity) increases if the introduction of the substituent diminishes the electronegativity of the nucleophile: $\Delta_x < 0$ if $\Delta\alpha > 0$. This conclusion is consistent with experiment (and the conclusion reached from the resonance model). An increase in basicity (occurring simultaneously with the decrease of electronegativity) is known to increase the reactivity of the nucleophile as a rule. An analogous conclusion has been reached[104] from thermochemical measurements, with the aid of which it was estimated whether the TS is close to either the reactants or products along the reaction coordinate: the TS moves towards the reactants with increase of the basicity of the nucleophile. The rate constants for the $RO^- + CH_3Cl$ gas-phase reactions with R = alkyl (Table 2) and for heteroatomic substituents are correlated with Taft $\sigma^*$ constants (in this case one should recall that gas-phase two-well potential curves introduce an additional uncertainty into the analysis). The most convincing confirmation of the conclusion concerning the character of the influence of the substituent in the nucleophile is provided by the correlation between the rate constants for the reaction

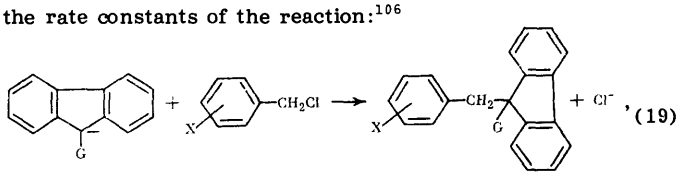


(18)

and the Hammett $\sigma$ constants for the substituents X [105] (X = $NH_2$, $CH_3O$, $CH_3$, Br, Cl, $CF_3$, OH, or $NO_2$). In this series the reaction rate varies by four orders of magnitude.[105]

(2) Substituent in the leaving group: $q_y - q_y^0 > 0$. In this case $\Delta y > 0$ for $\Delta\alpha > 0$. The reactivity diminishes if the substituent reduces the electronegativity of the leaving group (or increases its basicity), which agrees with the claim[104] that an increase in the basicity of the leaving group shifts the TS towards the products and also with the experimental observation that the nucleofugacity diminishes with increase of the basicity of the leaving group.

(3) Substituent at the central atom of the substrate: $q_c - q_c^0 > 0$ if $\beta_{cy}/\beta_0 > \varepsilon$ and $q_c - q_c^0 < 0$ if $\beta_{cy}/\beta_0 < \varepsilon$. In this case the reactivity series depends on the extent to which the C–Y bond in the TS is loosened compared with that in the initial state. The critical ratio of the resonance parameters is always less than unity. For the symmetrical case (X = Y), $\varepsilon = 2^{-\frac{1}{2}}$ (see Appendix 1). This estimate probably changes little when X ≠ Y if the main condition $\alpha_c \gg \alpha_x, \alpha_y$ remains in force. At any rate it is to be expected that the quantity $q_c - q_c^0$ is small in absolute magnitude, i.e. the effect of substituents must be appreciably weaker than in the first two cases. A linear correlation with the $\sigma$ constants of the substituents X is indeed observed for the rate constants of the reaction:[106]



, (19)

where G = phenyl, 2-benzenesulphonyl, CN, or $CH_3$. The rate constants for different X differ within the limits of 1–2 orders of magnitude. It then follows from the slope of the straight line that $q_c - q_c^0 > 0$. According to calculations by the MNDO method, $q_c - q_c^0 \approx 0.3$ e.s.u. for the $Cl^- + RCl$ systems.[73] The deviation of individual points from the correlation can probably be accounted for both by steric effects and by the inversion of the relation $\beta_{cy}/\beta_c \gtrless \varepsilon$: the lengths of the axial bonds vary within fairly wide limits as a function of the substituent—for example from 1.592 Å for R = F to 1.736 Å for R = OH in the TS $[HCH_2RH]^-$.[14] The reactivities estimated by calculation fit the Hammett correlation. This has been demonstrated in the case of the $Cl^- + XC_6H_4CH_2Cl$ reactions for which calculations were made by the CNDO/2 (X = $NH_2$, $CH_3$, F, $CF_3$, or $NO_2$) [107] and MNDO (X = F, OH, $OCH_3$, $NH_2$ or $NO_2$) [73] methods.

## 6. The Application of Correlation Equations

The relative reactivities of a series of nucleophiles (nucleophilicity) can be more or less satisfactorily described by a four-parameter equation of the Edwards type:[101,102]

$$\lg(k_x/k_{x_0}) = A(P_x - P_{x_0}) + B(H_x - H_{x_0}) , \quad (20)$$

where $P_x$ is a measure of the polarisability of the nucleophile, $H_x$ a measure of its basicity, linked directly to its proton affinity, and $X_0$ the standard nucleophile. More precisely the symbols X and $X_0$ correspond to the "nucleophile + solvent" pair, because the nucleophilicity depends on the solvent. Thus Eqn.(20) is suitable for the correlation of nucleophilicities in different solvents. The parameters *A* and *B* characterise the substrate and can be used in principle to correlate data for the relative mobilities of the leaving group Y (nucleofugacities).[102] Nevertheless, X and Y are involved in Eqn.(20) asymmetrically, i.e. the significance of the parameters *P* and *H* in relation to X is different from the significance of *A* and *B* in relation to Y.

For a complex anionic nucleophile $R^1X^-$ differing in the substituents in $R^-$, a relation of the Brønsted type holds satisfactorily:

$$\lg(k_x/k_{x_0}) = B[pK_a(X) - pK_a(X_0)] , \quad (21)$$

where $pK_a$ are the basicities of the corresponding nucleophiles. Linear correlations of type (21) have been found, for example, for the reactions of substituted fluorenyl and thiophenoxide anions with benzyl and butyl chlorides in DMSO [105,106] [systems (18) and (19)]. Eqn.(21) reduces to Eqn.(20) if the factors associated with the polarisability are constant in the reaction series. Other correlations (the Swain–Scott, Ritchie, etc. correlations) reduce similarly to Eqn.(20) when the reaction series are narrow.[102]

The reactivity in exchange reactions, including those of the $S_N2$ type, has been discussed in recent years on the basis of the Marcus equation:

$$U_{XY}^{\neq} = \lambda_{XY} - Q_{XY}/2 + Q_{XY}^2/16\lambda_{XY}$$
$$\lambda_{XY} = (\lambda_{XX} + \lambda_{YY})/2 \quad (22)$$

where $U_{XY}^{\neq}$ is the height of the potential barrier, identified with the observed activation energy, $Q_{XY}$ the heat of reaction ($Q_{XY} < 0$), and $\lambda_{XX} = U_{XX}^{\neq}$ and $\lambda_{YY} = U_{YY}^{\neq}$ are the barriers for thermally neutral symmetrical reactions. An analogous relation can be formulated also for the free energies $\Delta G_{XY}^{\neq}$, $\Delta G_{XX}^{\neq}$, and $\Delta G_{XY}^{\neq}$. Eqn.(22) was first used to describe the rearrangement of the solvation shells of transition metal ions in electron transfer reactions.[108,109] It was then applied to proton transfer reactions[110,111] and also to the transfer of the methyl group in the gas phase[40,41,112] and in solution.[113–115] Since the heat of reaction can be resolved into increments corresponding to X and Y, i.e. $Q_{XY} = Q_X + Q_Y$ (with an accuracy to within a constant independent of X and Y), it follows that Eqn.(22), like

Eqn.(20), is a four-parameter correlation. The Marcus equation is symmetrical relative to X and Y and, in contrast to Eqn.(20), embraces very wide series, including the variation of both the nucleophile and the leaving group. Its non-linearity makes it possible to explain the deviations from the linear Brønsted relations, which are sometimes observed.

The Marcus parameters differ fundamentally from the parameters of the usual correlations. The latter are normally associated with the electronic structures of the reactants in the spirit of the concept of the influence of the structures of the reactants on the reactivity. The parameters in Eqn.(22) are characteristics of the reactivity (or the PES) and not of the electronic structures of the reactants. From the standpoint of the concept indicated, they themselves require explanation. Nevertheless, they have a clear physical significance and in principle can be determined experimentally. The derivation of the Marcus equation from the overall PES for the exchange reactions is examined in Appendix 2.

For gas-phase $S_N2$ reactions, the Marcus equation has been used in the treatment of kinetic data obtained by the ICR method[40,41,112] and for the systematic treatment of several tens of liquid-phase reactions.[113-115] Its use is restricted by the insufficiency of experimental information about the heats $Q$ (especially in solution) and about the internal barriers $\lambda$. In the studies mentioned above, the quantities $\lambda_{XX}$ and $\lambda_{YY}$ were assumed to be adjustable parameters and were selected empirically ($\Delta G_{XX}$ in Table 6). If X and Y vary in the same series made up of $n$ members, then it is necessary to know $n$ values of the internal barrier $\lambda$ for the description of $n(n-1)/2$ asymmetric reactions. Since kinetic measurements have usually been made for by no means all asymmetric processes, the number of reference points exceeds only slightly the number of parameters. In this case the empirical adjustment of the latter is unreliable and ambiguous.

Table 6. The free energies of activation $\Delta G_{XX}$ in water[103] and the internal barriers $E_{XX}$ (calculation in terms of the 4-31G basis set[14]) for the symmetrical $X^- + CH_3X$ reactions.

| X | $\Delta G_{XX}$, kcal mol$^{-1}$ | $E_{XX}$, kcal mol$^{-1}$ |
|---|---|---|
| H | — | 57.3 |
| I | 23 | — |
| Br | 24 | — |
| Cl | 27 | 5.5 |
| F | 32 | 11.7 |
| $NO_2$ | 27 | — |
| TosO | 35 | — |
| $CH_3SO_3$ | 35 | — |
| $C_6H_5SO_3$ | 36 | — |
| $ClO_4$ | 37 | — |
| OH | 42 | 21.2 |
| CN | 51 | 28.5 |
| HS | — | 15.5 |
| HOO | — | 18 7 |
| FO | — | 18 8 |
| $CH_3O$ | — | 23.5 |
| $H_2N$ | — | 38 |
| NC | — | 43 8 |
| HCC | — | 50.4 |

The contribution of solvation to the activation barrier has been estimated from the Marcus equation in terms of the continuous polar medium model.[116-118] It was postulated that the reaction system moves along the chemical ("gas-phase") reaction coordinate $s$ up to a certain intermediate (not corresponding to a saddle point) value $s_0$. With $s_0$ fixed, the system is then moved along the coordinates of the medium, i.e. the solvent undergoes a rearrangement. The rearrangement is characterised by the reorganisation energy $E_R$ calculated from the electrostatic formula[93,108,109]

$$E_R = (\varkappa/2) \int \mathrm{d}V\,[D_1(s_0) - D_2(s_0)]^2 ,$$

where $\varkappa$ is the effective dielectric constant and $D_1$ and $D_2$ are the vectors of the electrical induction, generated by the charge distribution in the $X^- + CR_3Y$ chemical subsystem, which correspond to the initial and final states of the solvent for the fixed $s_0$. The integration is carried out over the entire space around the cavity occupied by the chemical subsystem. The estimates made for the simplest forms of the cavity[117,118] have shown that, in water with X = I and Y = F, Cl, or Br, the quantity $E_R$ varies from 60 to 80 kcal mol$^{-1}$. In this model the activation energy is

$$U^{\neq} = U(s_0) + [E_R/4 + Q(s_0)/2 + Q(s_0)^2/4E_R] .$$

The expression in square brackets describes the rearrangement of the solvent according to Eqn.(22); here the role of $\lambda_{XY}$ is assumed by the quantity $E_R/4$ and the modified heat $Q(s_0)$ characterises the rearrangement for a fixed $s_0$. Calculations by this formula have been compared with experiment for many $S_N2$ reactions in water and acetone[117,118] and the quantities $U(s_0)$ and $Q(s_0)$ were estimated from thermochemical and spectroscopic data.

Thus the contribution of the solvent to $\lambda_{XY}$ in Eqn.(22) can be expressed in terms of the reorganisation energy $E_R$. The contribution of the chemical rearrangement proper should be added to it, having calculated such contribution in terms of the internal barriers $\lambda_{XX}$ and $\lambda_{YY}$ in Eqn.(22).

Quantum-chemical calculations of the internal barriers are of undoubted interest in this connection (Table 6). Systematic quantum-chemical study of the PES for simple $S_N2$ reactions[14,59] made it possible to check how well the Marcus equation holds by comparing directly its predictions with the calculated potential barriers. For the description of reactions between electrostatic complexes, $[X^-.CH_3Y] \rightarrow [XCH_3.Y^-]$, the agreement proved to be very satisfactory in the case of 11 X,Y reaction pairs: H, NC; H, CN; H, F; H, CCH; H, OH; F, SH; HO, CN; HO, F; HCC, F; F, OOH; $CN^-$, F. The height of the barriers was varied within the limits of 50 kcal mol$^{-1}$. In order to describe the entire two-well potential curve, Eqn.(22) was modified.[14]

It is noteworthy that both the calibration of the Marcus equation and its comparison with the exact calculation have been carried out on the basis of energetically unreliable calculations in terms of the 4-31G basis set. Nevertheless, the fact that this equation describes satisfactorily model quantum-chemical PES over a very wide energy range indicates the possibility of applying it to real $S_N2$ reactions. This is apparently the only way of treating systematically wide reaction series with different X and Y within the framework of a simple correlation scheme.

As already mentioned (Section III), simpler schemes, such as the Bell–Evans–Polanyi equation (linear dependence of the activation energy on the heat of reaction) and the Brønsted equation (the analogous relation for free energies) are applicable to a reaction series with variable X or Y. Satisfactory Brønsted relations can be observed only by varying the substituent with a constant reaction centre. Linear relations (21) reduce to Brønsted relations if it is assumed that the heats of reaction $Q$ are linearly related to the basicities of the nucleophiles. Comparison of the calculated affinities of nucleophiles for the proton and the methyl cation[14] demonstrated the likelihood of this hypothesis. Thus one may conclude that Brønsted correlations exist for systems (18) and (19) in DMSO with the reaction rate

constants varying in the range of 4–5 orders of magnitude[105,106] (~10 kcal mol$^{-1}$ on the energy scale). A similar conclusion was reached in the study of other systems.[119,120] The absence of a visible curvature in the Brønsted plots within the framework of the Marcus equation shows that the role of the quadratic term in Eqn.(22) is small, i.e. that the ratio $Q_{XY}/\lambda_{XY}$ is small. It is of interest that this holds against the background of fairly large systematic changes in the structure of the TS (Table 5). In other words, the derivation of linear relations from equations of type (20), always based on the implicit assumption that the reaction centre is constant, is not convincing.

According to an alternative view,[105] over such a wide range of variation of the reactivity, the Marcus curvature should have been manifested and the linearity of the observed correlations is therefore a special effect whose nature is still obscure and at any rate cannot be accounted for within the framework of the Marcus equation.

It may be that there are systematic deviations from Brønsted correlations. An anomalous increase of reactivity has been observed for a heteroatomic substituent with an unshared electron pair in the nucleophile. The corresponding positive deviations from the Brønsted relation have been called the α-effect.[121–123] In solution the α-effect for $S_N2$ reactions is weak.[123] Measurements in the gas phase for the $X^-$ + $CH_3F$ reactions (X = OH or OOH) led to the conclusion that this effect is absent.[124] Calculation of the heights of the barriers and heats of the $X^-$ + $CH_3F$ reactions (X = HO, $CH_3O$, HOO, FO, or HCOO) in terms of the 4-31G basis set[14,19] yielded ambiguous results: a satisfactory linear relation can be drawn through these five points. The calculation also failed to reveal anomalies in the geometrical structure of the TS for reactions with α-substituted nucleophiles (Tables 4 and 5) and also in the energy relations for symmetrical reactions (Tables 4 and 6). The authors[14,99] are therefore inclined to assume that in the gas phase the α-effect is absent for $S_N2$ reactions and its existence in solution is due to differences between the solvation energies of the normal and α-substituted nucleophiles. Reliable data are apparently still insufficient at the present time for the final solution of this problem.

Attempts to improve the Marcus equation for $S_N2$ reactions have been published.[125,126] The shifts of the TS in the reaction series not only along the reaction coordinate but also at right angles to it have been considered in these models. In other words, a change in the reaction pathway curve for the reaction series is permitted. Additional empirical parameters appear in the corresponding correlation equations which makes the practical application of such equations relatively ineffective.

## IV. APPENDICES

### Appendix 1

Analysis of the sign of the quantity $\Delta q_i = q_i - q_i^0$ subject to the condition $\alpha_c \gg \alpha_x, \alpha_y$.

(1) Substitution at the nucleophile.

Here $q_x^0 = 2$ and $1 < q_x < 2$ [127] as a consequence of the partial delocalisation of the unshared electron pair. Thus, $\Delta q_x > 0$.

(2) Substitution at a carbon atom.

In this case $0 < q_c^0 < 1$ and $0 < q_c < 1$, so that the analysis is more complex. We shall carry it out for the symmetrical X–C–X system assuming that the results do not change greatly for X ≠ Y, provided that $\alpha_c \gg \alpha_x, \alpha_y$.

It is possible to introduce the group orbitals $|x_+\rangle = (|x_1\rangle \pm |x_2\rangle)/2^{1/2}$, where $|x_1\rangle$ and $|x_2\rangle$ are the atomic orbitals of different atoms X. The corresponding matrix elements are equal (for the significance of the notation, see Section III):

$$\langle x_+|h|x_+\rangle = \langle x_-|h|x_-\rangle = \alpha_x \ ;$$
$$\langle x_+|h|c\rangle = 2^{1/2}\langle x|h|c\rangle = 2^{1/2}\beta_{cx} \ ;$$
$$\langle x_-|h|c\rangle = 0 \ .$$

As a consequence of symmetry, only one lowest MO of the X–C–X system is bonding; the MO which follows it is non-bonding and does not contribute to $q_c$. The lowest MO can be formulated thus:

$$\psi_1 = c_{11}|c\rangle + c_{12}|x_+\rangle$$

and the MO which follows it can be written as follows:

$$\psi_2 = c_{21}|c\rangle + c_{22}|x_-\rangle \ .$$

The coefficients of $\psi_1$ are found from the secular equation for a quasi-two-centre "bond":

$$\underset{\alpha_c}{C} \overset{2^{1/2}\beta_{cx}}{\text{———}} \underset{\alpha_x}{X_+} \ .$$

In the initial state a two-centre bond is considered (see Section III):

$$\underset{\alpha_c}{C} \overset{\beta_0}{\text{———}} \underset{\alpha_x}{X} \ .$$

These bonds differ formally only by the value of the resonance integral. We thus obtain

$$\Delta q_c > 0, \quad \text{if} \quad \beta_{cx}/\beta_0 > 1/2^{1/2} \ ;$$
$$\Delta q_c < 0, \quad \text{if} \quad \beta_{cx}/\beta_0 < 1/2^{1/2} \ .$$

(3) Substitution at the leaving group.

An unambiguous conclusion can be reached most simply for the symmetrical situation X = Y examined above. It is sufficient to use the symmetry condition $q_x = q_y$ and the normalisation condition $q_x + q_c + q_y = 4$. Then $q_y = 2 - q_c/2$. In the initial state $q_y^0 = 2 - q_c^0$ according to the normalisation condition. Hence $\Delta q_y = q_c^0 - q_c/2$. This quantity is known to be positive when $\Delta q_c < 0$ (i.e. $\beta_{cx}/\beta_0 < 2^{-1/2}$). In the general case the difference between $q_c$ and $q_c^0$ is small ($q_c/q_c^0 \cong 1$), so that the relation $\Delta q_y > 0$ always holds.

### Appendix 2. The Marcus Equation

The canonical Marcus formula for the height of the chemical reaction barrier has the form of Eqn.(22), where $Q_{XY}$ is the heat of reaction and $\lambda_{XY}$ the so-called "internal barrier". It was obtained for electron transfer reactions,[108,109] whose PES were modelled by two intersecting paraboloids. The derivation of Eqn.(22) has been revised[110] in relation to the usual reactions with rearrangement of chemical bonds, for which the parabolic approximation of the PES is far from realistic. Subsequently it was modified by various investigators.[128–133]

Eqn.(22), which establishes a non-linear relation between the height of the potential barrier and the heat of reaction, can be obtained as a consequence of simple geometrical properties of PES of a specific type. In the derivation given below, this factor is specially emphasised.

Fig.6a illustrates schematically the two-dimensional c curve—the coordinate of a typical exchange reaction. The points $s_1$ and $s_2$, corresponding to the reactants and products, are selected on it (these can be electrostatic or

van der Waals minima; in principle, it is sufficient to choose any points in the asymptotic regions of the reactants or products, where the reaction coordinate becomes a straight line). Suppose that $\sigma$ is the length of the arc $ss_1$ linked to the current coordinate s on the c curve and $\sigma_0$ is the length of the arc $s_2s_1$. The variable $\alpha = \sigma/\sigma_0$ is a natural characteristic of the movement of the system from the reactants to the products on the PES.

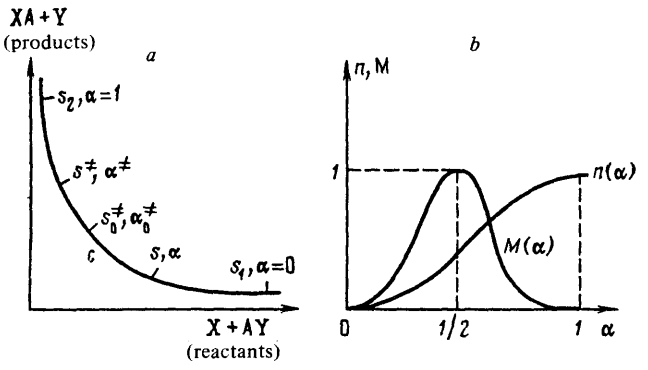



**Figure 6.** Illustration of the derivation of the Marcus equation: *a*) the $S_N2$ reaction coordinate; *b*) kinetic [$M(\alpha)$] and thermodynamic [$n(\alpha)$] interpolation functions; $\alpha = (s - s_1)/(s_2 - s_1)$.

The PES profile $U(\alpha)$ is represented by the relation

$$U(\alpha) = n(\alpha)U(1) + \lambda M(\alpha);\ U(1) = Q \qquad (23)$$

The interpolation functions $n(\alpha)$ and $M(\alpha)$ are specified in the following form (see Fig. 6*b*):

$$\begin{aligned} &0 \leqslant n(\alpha) \leqslant 1;\ n(0) = 0;\ n(1) = 1;\ n(1/2) = 1/2;\ dn/d\alpha > 0 \\ &0 \leqslant M(\alpha) \leqslant 1;\ M(0) = M(1) = 0;\ M(1/2) = 1;\ \frac{dM}{d\alpha}(1/2) = 0; \end{aligned} \qquad (24)$$

$$\frac{d^2M}{d\alpha^2}(1/2) = -k < 0 \qquad (25)$$

According to these definitions, both functions are normalised to unity, $n(\alpha)$ increases monotonically and $M(\alpha)$ has a single maximum at $\alpha = 1/2$. The $U(\alpha)$ potential curve is divided into two components: one component (the "thermodynamic contribution") describes the monotonic evolution of heat and the other (the "kinetic contribution") is responsible for the barrier. The main hypothesis is that $n(\alpha)$ and $M(\alpha)$ are the same in the reaction series, i.e. are the same for all X and Y. Eqns.(24) and (25) do not impose serious limitations on the choice of these functions (with the exception of the symmetrical choice of the value of n at the point $\alpha = 1/2$—a condition which is discussed below). The methods of their detailed specification discussed in the literature[129,130,132] are always arbitrary and are unsuitable for further treatment.

The quantity $U(1)$ is the heat change and $\lambda$ is determined from Eqn.(23) for symmetrical reactions [X = Y: $U_{XX}(1) = 0$]:

$$U_{XX}(1/2) = U^{\neq}_{XX} = \lambda_{XX}\ . \qquad (26)$$

The following approximation has been adopted for asymmetric reactions:[110]

$$\lambda_{XY} = (U^{\neq}_{XX} + U^{\neq}_{YY})/2\ . \qquad (27)$$

Subsequently the function (23) is expanded in Taylor's series in the vicinity of the point $\alpha = 1/2$ and the position of the maximum $\alpha^{\neq}$ is found taking into account the quadratic terms of the expansion on the basis of the condition

$$\left.\frac{dU}{d\alpha}\right|_{\alpha^{\neq}} = 0\ . \qquad (28)$$

Elementary calculations using Eqns.(23)–(25) yield

$$U^{\neq} = U(\alpha^{\neq}) = \lambda + U(1)/2 + (n')^2[U(1)]^2/2k\lambda\ , \qquad (29)$$

where

$$n' = \frac{dn}{d\alpha}(1/2)\ .$$

This is the generalised Marcus formula. The canonical formula (22) is obtained from the latter by putting $(n')^2/k = 1/8$. This result is obtained if the PES profile has the form of two intersecting parabolas.[108] According to the above derivation, the quantity $(n')^2/k$ is a characteristic of the interpolation functions $n(\alpha)$ and $M(\alpha)$, which should be selected in such a way that the PES profile is reproduced most effectively for the given reaction series. In an empirical treatment, $(n')/k$ should be regarded as an adjustable parameter. The special selection of Eqn.(22) usually made has persisted partly because of inertia but mainly because it proved to be fairly apt by chance. The coefficient 1/2 of the linear term in Eqn.(29) is obtained on the assumption that $n(1/2) = 1/2$, which is also non-obligatory. It arose as a consequence of the selection of the symmetrical reaction (X = Y) as the standard around which the expansion in Taylor's series is carried out. If reaction series with highly asymmetric TS are studied, it is more convenient to assume that the quantity $n(1/2)$ is yet another adjustable parameter and to calibrate it against data for any reaction chosen as the standard (the choice $\alpha = 1/2$ is permissible for any standard reaction, which need not necessarily be symmetrical). Such treatment of various series of reactions involving the radical abstraction of hydrogen yielded $n(1/2) = 0.54$–$0.7$.[131]

The non-linearity of Eqn.(29) appeared as a consequence of the variation of the positions of the TS on the reaction coordinate in conformity with the condition for a stationary state [Eqn.(28)]. In linear correlations of the Hammett type, the constancy of the structure of the TS throughout the reaction series is always implied. The same hypothesis is implicit in various approximate quantum-chemical treatments. The fact that the structure of the TS is not postulated but is calculated by a physically well-founded procedure is the fundamental feature distinguishing the Marcus equation among other theories of reactivity.

The shift of the TS along the reaction coordinate is described by the expression

$$\alpha^{\neq} - 1/2 = n'U(1)/k\lambda\ . \qquad (30)$$

For each specific reaction, it is controlled by the ratio of the heat of reaction and the energy of the internal barrier. The shift is appreciable in reaction series with a small force constant *k*—a situation which is characteristic of exchange reactions in which the TS is symmetrical or almost symmetrical and the reaction coordinate is an antisymmetric mode. The application of the Marcus equation to such reactions (these include also the $S_N2$ reactions) is most fruitful. On the other hand, in reactions involving addition to a multiple bond, where the reaction coordinate virtually coincides with the contraction along the newly formed bond, the force constant is large and the shift defined by Eqn.(30) is negligible.[134] In this case Eqn.(29) becomes linear with an unjustifiably rigidly fixed value of 1/2 for the Brønsted coefficient.

According to this derivation, the shifts defined by Eqn.(30) should not be very large. This is why the use of a symmetrical standard reaction [$n(1/2) = 1/2$] for the description of highly asymmetric TS yields unsatisfactory results.

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# Kinetics and Mechanism of Electron Transfer in Proteins

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The results of studies on the kinetics of the oxidation-reduction reactions of individual proteins (electron transfer agents and enzymes) are described. Attention has been concentrated on the effect of the nature of the active centres in the protein molecules and of the modification of individual aminoacid residues on the rate of electron transfer in a homogeneous medium. Questions associated with the electrochemical reactions of proteins and with the effect of the state of the interface on the rate of this process are considered in detail. Ideas concerning the theoretical calculation of the rate constants for electron transfer in proteins are described.
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## I. INTRODUCTION

The oxidation-reduction processes involving the synthesis and degradation of substances in living organisms are effected with participation of protein systems in which electron transfer takes place via the oxidation or reduction of active centres in the protein molecules.[1] The success of the practical employment of these reactions, which is now beginning to take shape, in the transformation of organic and inorganic compounds, in energy conversion, and in electrocatalytic systems[2-4] is to a large extent determined by the depth of our understanding of the principal characteristics of electron transfer in individual proteins. The quantitative estimation of the rate of electron transfer in proteins assumes no less importance in the modelling of enzyme catalysis and in the creation of effective low-molecular-weight catalysts.[5] The kinetics of the oxidation-reduction reactions of individual proteins are also of considerable theoretical interest for molecular biology and related fields, because they help in understanding the mechanism of the functioning of oxidation-reduction electron transfer chains in biological membranes.

Kinetic studies occupy at present a permanent place in the research into the mechanism of electron transfer in proteins. The development of preparative methods, which make it possible to obtain individual proteins in amounts necessary for chemical experiments, promoted the rapid accumulation of experimental data concerning the influence of the structure of the protein globule or even of individual aminoacids on the rate of electron transfer. A survey and discussion of these results appear to be extremely timely.

The present review is devoted to the analysis of the kinetic results of studies on the oxidation-reduction reactions of proteins—electron transfer agents and enzymes. It presents data on the chemical and electrochemical reactions of proteins and describes the principal ideas concerning the theoretical calculation of the rate of electron transfer.

## II. OXIDATION-REDUCTION REACTIONS OF ELECTRON TRANSFER AGENTS

### 1. The Formal Kinetic Features of Electron Transfer in Proteins

Oxidation-reduction proteins which are components of the oxidation-reduction electron transfer chains or which participate in oxygen transport processes as a rule have low molecular weights and contain metals, iron–sulphur clusters, flavin-adenine dinucleotide (FAD), flavin mononucleotide (FMN), or other co-factors in the active centre. After isolation in the native state, these proteins are able to react with various compounds and such reactions are bimolecular.

Since protein molecules are charged species, the rate of the process depends on the electrostatic interactions. In order to eliminate this effect, the rate constant is referred to infinite ionic strength of the solution in accordance with the expression:[6]

$$\ln k^{\infty} = \ln k + 3.576 \left[\frac{\exp(-\kappa R_1)}{1+\kappa R_2} + \frac{\exp(-\kappa R_2)}{1+\kappa R_1}\right]\left[\frac{Z_1 Z_2}{R_1+R_2}\right],$$

in which $Z_1$, $Z_2$, $R_1$, and $R_2$ are respectively the charges and radii of the reacting molecules and $\kappa = 3.29\ \mu^{1/2}\ \text{nm}^{-1}$ (25 °C), where $\mu$ is the ionic strength of the solution expressed as a molarity.

The rate constants for the bimolecular reactions of electron transfer agents with complexes vary in the range $10^6$–$10^{-2}$ litre $\text{mol}^{-1}\ \text{s}^{-1}$ and depend on the pH, the ionic strength of the solution, and on the nature of the donor and acceptor. Analysis of the data presented in Table 1 shows that inorganic reactants containing aromatic ligands react at a higher rate than coordination compounds of the same metals without hydrophobic ligands. The reactivity of cobalt oxalate complexes is as a rule low. Low rate constants are also observed for proteins whose physiological function consists in transporting oxygen, namely for haemoglobin and myoglobin.

**Table 1.** The rate constants and certain thermodynamic parameters of the reactions of electron transferring agents with inorganic complexes at 25 °C.

| Oxidant | Reductant | pH | μ, M | $k_{12}$, litre mol$^{-1}$ s$^{-1}$ | $\Delta H^{\neq}$, kJ mol$^{-1}$ | $\Delta S^{\neq}$, J mol$^{-1}$ K$^{-1}$ | Refs |
|---|---|---|---|---|---|---|---|
| $Ru(NH_3)(pyr)^{3+}$ | Azurin | 6.5 | 0.1 | $2.0\cdot10^3$ | 41.1 | —58.7 | [7] |
| $Ru(pyr)_3^{2+*}$ | " | 7.0 | 0.1 | $6.9\cdot10^8$ | — | — | [8] |
| $Co(ox)_3^{3-}$ | " | 7.0 | 0.5 | $2.9\cdot10^{-2}$ | — | — | [9] |
| $Co(phen)_3^{3+}$ | " | 7.0 | 0.1 | $3.2\cdot10^3$ | 59.9 | 20.9 | [10] |
| $Co(5,6\text{-}Me_2\text{-}phen)_3^{3+}$ | " | 7.0 | 0.1 | $1.5\cdot10^3$ | 48.6 | —20.9 | [10] |
| $Co(5\text{-}Cl\text{-}phen)_3^{3+}$ | " | 7.0 | 0.1 | $4.2\cdot10^2$ | 37.3 | —71.2 | [10] |
| $Co(4,7\text{-}Me_2\text{-}phen)_3^{3+}$ | " | 7.0 | 0.1 | $8.4\cdot10^1$ | 41.5 | —71.2 | [10] |
| Azurin | $Fe(EDTA)^{2-}$ | 7.0 | 0.2 | $1.3\cdot10^3$ | 8.4 | —155 | [11] |
| $Co(phen)_3^{3+}$ | Plastocyanin | 7.0 | 0.1 | $4.9\cdot10^3$ | 58.7 | 20.9 | [10] |
| ditto | ditto | 7.0 | 0.5 | $1.0\cdot10^3$ | — | — | [9] |
| " | " | 7.0 | 0.1 | $3.9\cdot10^2$ | 40.6 | —61.2 | [12] |
| $Ru(pyr)_3^{2+*}$ | " | 7.0 | 0.1 | $1.6\cdot10^9$ | — | — | [8] |
| $Co(5,6\text{-}Me_2\text{-}phen)_3^{3+}$ | " | 7.0 | 0.1 | $8.0\cdot10^3$ | 57.0 | 4.2 | [10] |
| $Co(5\text{-}Cl\text{-}phen)_3^{3+}$ | " | 7.0 | 0.1 | $7.0\cdot10^2$ | 45.7 | —33.5 | [10] |
| $Co(4,7\text{-}Bs_2\text{-}phen)_3^{3-}$ | " | 7.0 | 0.1 | $2.6\cdot10^1$ | 32.7 | —10.9 | [10] |
| $Co(ox)_3^{3-}$ | " | 7.0 | 0.5 | $2.4\cdot10^{-1}$ | — | — | [9] |
| $Ru(NH_3)_4(pyr)^{3+}$ | " | 6.5 | 0.1 | $2.0\cdot10^3$ | — | — | [7] |
| Plastocyanin | $Fe(EDTA)^{2-}$ | 7.5 | 0.2 | $3.1\cdot10^4$ | — | — | [11] |
| ditto | ditto | 5.5 | 0.2 | $5.5\cdot10^4$ | — | — | [11] |
| " | $Ru(NH_3)_6^{2+}$ | 7.0 | 0.1 | $2.4\cdot10^6$ | — | — | [12] |
| $Ru(NH_3)_4(pyr)^{3+}$ | Stellacyanin | 6.5 | 0.1 | $1.9\cdot10^5$ | 28.1 | —50.3 | [7] |
| $Ru(pyr)_3^{2+}$ | ditto | 7.0 | 0.1 | $4.2\cdot10^8$ | — | — | [8] |
| $Co(phen)_3^{3+}$ | " | 7.0 | 0.5 | $1.8\cdot10^5$ | — | — | [9] |
| $Co(ox)_3^{3-}$ | " | 7.0 | 0.5 | $7.3\cdot10^2$ | — | — | [9] |
| $Co(5,6\text{-}Me_2\text{-}phen)_3^{3+}$ | " | 7.0 | 0.1 | $1.8\cdot10^4$ | 38.5 | —29.3 | [10] |
| $Co(4,7\text{-}Bs_2\text{-}phen)_3^{3-}$ | " | 7.0 | 0.1 | $2.3\cdot10^6$ | 24.7 | — | [10] |
| Stellacyanin | $Fe(EDTA)^{2-}$ | 7.5 | 0.5 | $5.1\cdot10^5$ | — | — | [11] |
| ditto | ditto | 5.0 | 0.5 | $5.7\cdot10^5$ | — | — | [11] |
| " | $Fe(CN)_6^{4-}$ | 6.0 | 0.1 | $1.6\cdot10^3$ | — | — | [13] |
| $Ru(NH_3)_4(pyr)^{3+}$ | Cytochrome *c* | 5.3 | 0.5 | $1.9\cdot10^4$ | 35.2 | —46.1 | [7] |
| $Co(ox)_3^{3-}$ | ditto | 7.0 | 0.5 | 5.5 | — | — | [9] |
| $Co(pic)_2^{3+}$ | " | 7.0 | 0.2 | $1.1\cdot10^4$ | 18.4 | —10.5 | [14] |
| $Co(phen)_3^{3+}$ | " | 7.0 | 0.1 | $1.5\cdot10^3$ | 47.3 | —25.1 | [15] |
| $Co(5\text{-}Cl\text{-}phen)_3^{3+}$ | " | 7.0 | 0.1 | $1.3\cdot10^2$ | 40.2 | —67.0 | [15] |
| $Co(5,6\text{-}Me_2\text{-}phen)_3^{3+}$ | " | 7.0 | 0.1 | $2.7\cdot10^2$ | 51.9 | —25.1 | [15] |
| $Co(4,7\text{-}Me_2\text{-}phen)_3^{3+}$ | " | 7.0 | 0.1 | $2.8\cdot10^1$ | 61.2 | —12.6 | [15] |
| $Co(4,7\text{-}Bs_2\text{-}phen)_3^{3-}$ | " | 7.0 | 0.1 | $2.9\cdot10^3$ | 53.6 | — | [15] |
| Cytochrome *c* | $Fe(pic)_2^{2-}$ | 7.0 | 0.2 | $1.5\cdot10^4$ | 30.2 | —64.5 | [14] |
| ditto | $Ru(NH_3)_6^{2+}$ | 6.1 | 0.1 | $3.8\cdot10^4$ | — | — | [16] |
| " | $Fe(EDTA)^{2-}$ | 7.0 | 0.09 | $9.0\cdot10^3$ | — | — | [17] |
| $Fe(CN)_6^{3-}$ | Cytochrome $c_{551}$ | 7.0 | 0.1 | $1.0\cdot10^2$ | — | — | [18] |
| $Co(phen)_3^{3+}$ | ditto | 7.0 | 0.1 | $5.3\cdot10^4$ | 51.5 | 16.8 | [15] |
| $Co(5\text{-}Cl\text{-}phen)_3^{3+}$ | Cytochrome $c_{551}$ | 7.0 | 0.1 | $4.4\cdot10^3$ | 39.4 | —41.9 | [15] |
| $Co(5,6\text{-}Me_2\text{-}phen)_3^{3+}$ | ditto | 7.0 | 0.1 | $4.3\cdot10^3$ | 57.0 | 29.3 | [15] |
| $Co(4,7\text{-}Me_2\text{-}phen)_3^{3+}$ | " | 7.0 | 0.1 | $3.2\cdot10^3$ | 45.7 | —25.1 | [15] |
| $Co(4,7\text{-}Bs_2\text{-}phen)_3^{3-}$ | " | 7.0 | 0.1 | $2.8\cdot10^4$ | 57.8 | 33.5 | [14] |
| $Co(pic)_3$ | " | 7.0 | 0.2 | $5.8\cdot10^2$ | 15.1 | —142.5 | [14] |
| Cytochrome $c_{551}$ | $Fe(pic)_2^{2-}$ | 7.0 | 0.2 | $3.2\cdot10^5$ | 40.2 | —41.9 | [19] |
| Cytochrome $b_5$ | $Fe(EDTA)^{2-}$ | 7.0 | 0.5 | $2.8\cdot10^2$ | 22.6 | —122.3 | [19] |
| Cytochrome *c* $d_1$ (haem *c*) | ditto | 7.0 | 0.5 | $2.0\cdot10^2$ | — | — | [20] |
| Cytochrome *c* $d_1$ (haem $d_1$) | " | 7.0 | 0.5 | $0.6\cdot10^2$ | — | — | [20] |
| Methaemoglobin | " | 7.0 | 0.2 | $2.9\cdot10^1$ | 23.0 | —138 | [21] |
| Methaemoglobin | " | 7.0 | 0.2 | $3.1\cdot10^1$ | 50.3 | —54.3 | [21] |
| ditto | " | 6.3 | 0.15 | $3.1\cdot10^1$ | — | — | [22] |
| " | $Co(sep)^{2+}$ | 6.3 | 0.15 | $3.5\cdot10^3$ | — | — | [22] |
| " | $SO_3^-$ | 6.3 | 0.15 | $4.5\cdot10^6$ | — | — | [22] |
| $Co(ox)_3^{3-}$ | HPIP | 6.3 | 0.5 | $8.0\cdot10^{-3}$ | — | — | [9] |
| $Co(phen)_3^{3+}$ | ditto | 6.3 | 0.1 | $2.8\cdot10^3$ | 62.4 | 30.2 | [23] |
| $Fe(CN)_6^{4-}$ | " | 6.3 | 0.08 | $(0.2\text{–}5)\cdot10^4$ | — | — | [24] |
| HPIP | $Fe(EDTA)^{2-}$ | 7.0 | 0.1 | $1.6\cdot10^3$ | 3.3 | —171.8 | [23] |
| Rubredoxin | $Ru(NH_3)_6^{2+}$ | 7.0 | 0.1 | $9.5\cdot10^4$ | 5.9 | —129.9 | [25] |
| ditto | $V(H_2O)_6^{2+}$ | 4.0 | 0.1 | $1.6\cdot10^4$ | 0.4 | —167.6 | [25] |
| " | $Cr(H_2O)_6^{2+}$ | 4.0 | 0.1 | $1.2\cdot10^3$ | 0.4 | —184.4 | [25] |
| Ferredoxin | V(EDTA)$^{2-}$ | 7.3 | 0.05 | $3.0\cdot10^4$ | 23.5 | —88.0 | [26] |
| | Eu(PTDA)$^{3-}$ | 7.3 | 0.05 | $3.2\cdot10^5$ | 352.0 | —29.3 | [26] |
| $Fe(CN)_6^{3-}$ | Cytochrome *f* | 7.0 | 0.05 | $1.7\cdot10^5$ | 3.6 | —159.2 | [27] |

Notation: EDTA = ethylenediaminetetra-acetate; PDTA = 1,2-diaminopropanetetra-acetate; pyr = pyridine; ox = oxalate; pic = 2,6-dipicolinate; phen = 1,10-phenanthroline; 5-Cl-phen = 5-chloro-1,10-phenanthroline; 4,7-$Me_2$-phen = 4,7-dimethyl-1,10-phenanthroline; 5,6-$Me_2$-phen = 5,6-dimethyl-1,10-phenanthroline; 4,7-Bs-phen = 4,7-di-(benzenesulphonyl)-1,10-phenanthroline; sep = 1,3,6,8,10,13,16,19-octa-azabicyclo[6.6.6]eicosane; HPIP = high-potential iron-containing protein.

*Electronically excited.

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

The enthalpies and entropies of activation of electron transfer reactions vary from 0 to 352 kJ mol$^{-1}$ and from −185 to 33 J mol$^{-1}$ K$^{-1}$ respectively, which indicates the possibility of appreciable conformational changes in the protein globules on electron transfer, because low activation enthalpies are typical for the formation of simple bimolecular collision complexes, while the activation entropy is −40 J mol$^{-1}$ K$^{-1}$.

A species specificity is also manifested in electron transfer reactions. The high-potential iron-containing protein plastocyanin isolated from various sources reacts with different oxidants at unequal rates. At a low ionic strength, certain transfer agents form complexes with inorganic ions. The stability constant of the complex of azurin with the phenanthroline complex of cobalt is 457 litre mol$^{-1}$, while the rate constant for the reaction is $k$ = 21.3 s$^{-1}$.[28] The reaction between the same copper-containing protein and hexacyanoferrate(III) proceeds in a more complex manner with formation of complexes of both oxidised and reduced azurin.[29] The oxidation of cytochrome *c* with hexacyanoferrate(III) also leads to the formation of a complex whose stability constant is $3.2\times10^4$ litre mol$^{-1}$, while the reaction rate constant is $1.9\times10^3$ s$^{-1}$.[30]

The effect of pH on the rate of the process is determined by the change in the degree of protonation of the aminoacid residues in the region of the centres of proteins. It has been shown that the deprotonated histidine residue His-83 in the azurin molecule decreases the electrostatic repulsion of positively charged ions, so that at pH's above the p$K$ there is an appreciable increase of the reaction rate.[28] In reactions with hexacyanoferrate, His-35 is responsible for the binding of the substrate and its protonation in an acid medium appreciably accelerates the process. In the case of plastocyanin at pH < 5, the rate of reaction is appreciably reduced when the phenanthroline complex of cobalt is used, but is independent of pH when negatively charged complexes are employed.[10] This is because the phenanthroline complex binds to the deprotonated Tyr-83 residue located at a distance of 1 nm from the active centre, while hexacyanoferrate(III) forms a complex with deprotonated His-87 (p$K$ = 5.7) located in the coordination sphere of copper.[31] Since the protonated Lys-72 and Lys-13 residues present near the haem group participate in the reactions of cytochrome *c* with hexacyanoferrate and other negatively charged reagents,[32] the association of cytochrome *c* with polyamines reduces the reaction rate. The rate of reaction is also influenced by the protonation of Tyr-87, which is responsible for conformational changes in the protein globule.[16]

Redox proteins exhibit overall an increased reactivity in relation to organic compounds (Table 2). Particularly large rate constants for the reduction of proteins have been observed in their reactions with the radical-cations of viologens and other radical species. The rate of reaction of flavodoxin, cytochrome *c*, and cytochrome $c_3$ with the methylviologen radical-cation approaches the rate of a diffusion-controlled process. Reduced flavin mononucleotide ($FMNH_2$) and its semiquinone ($FMNH^{\bullet}$) are also highly reactive owing to their low redox potentials.

It has been shown that the electron transfer in the reactions of cytochrome *c* with flavins takes place when the *N*-5-region in the flavin molecules is oriented towards the haem gap, while the *N*-pyrimidine component is oriented in the opposite direction.[34] The rigorous relative disposition of the reactants in the collision complex is responsible for the weak dependence of the reaction rate on the ionic strength of the solution despite the fact that $FMNH^{\bullet}$ and $FMNH_2$ have charges of −2 and −2.8 respectively. The results obtained are important for the theoretical analysis

of the dependence of the rate of electron transfer on the ionic strength of the solution.

The rate of reaction of the solvated electron with cytochrome *c*, myoglobin, and methaemoglobin is determined by diffusion.[41,42] The redox state of the active centre has little influence on the rate of reduction of the protein and only the removal of haem from mylglobin retards the rate of reaction by a factor of two.

Table 2. The rate constants for the interaction of redox proteins with organic compounds (25 °C).

| Protein | Reductant | pH | μ, M | $k_{12}$, litre mol$^{-1}$ s$^{-1}$ | Refs. |
|---|---|---|---|---|---|
| Cytochrome *c* | $FMNH^{\cdot}$ | 7.0 | 0.01 | $6.0\cdot10^7$ | [33] |
| | $FMNH^{\cdot}$ | 7.0 | 0.1 | $7.0\cdot10^7$ | [34] |
| | $FMHH_2$ | 7.0 | 0.1 | $3.0\cdot10^7$ | [34] |
| | 2-Methyl-1,4-naphthohydroquinone | 6.0 | 0.1 | $8.5\cdot10^2$ | [35] |
| | Tetrachloro-1,4-hydroquonone | 7.4 | 0.02 | $4.2\cdot10^5$* | [36] |
| | Tetramethylphenylenediamine | 7.4 | 0.02 | $2.6\cdot10^4$* | [36] |
| | *N*-Methylhydrophenazine | 7.4 | 0.02 | $6.0\cdot10^5$* | [36] |
| | $MV^+$ | 7.0 | 0.004 | $7.2\cdot10^7$* | [37] |
| | $C_2H_5OH^{\cdot}$ | 7.0 | 0.004 | $1.4\cdot10^8$* | [37] |
| | $MV^+$ | 7.0 | 0.2 | $2.3\cdot10^8$* | [37] |
| | $MV^+$ | 7.2 | 0.07 | $2.4\cdot10^7$ | [38] |
| | $BV^+$ | 7.2 | 0.07 | $3.3\cdot10^7$ | [38] |
| Cytochrome $c_3$ | $MV^+$ | 7.2 | 0.005 | $4.5\cdot10^8$* | [37] |
| | $C_2H_5OH^{\cdot}$ | 7.2 | 0.005 | $6.0\cdot10^8$* | [37] |
| | $MV^+$ | 7.2 | 0.3 | $9.7\cdot10^8$* | [37] |
| Methaemoglobin | $FMNH_2$ | 7.0 | 0.1 | $5.5\cdot10^6$ | [39] |
| Metmyoglobin | $MV^+$ | 7.0 | 0.004 | $2.3\cdot10^7$* | [37] |
| | $C_2H_5OH^{\cdot}$ | 7.0 | 0.004 | $5.5\cdot10^7$* | [37] |
| | $MV^+$ | 7.0 | 0.2 | $5.4\cdot10^7$* | [37] |
| | Ascorbate anion | 7.2–8.1 | 0.3 | $1.2\cdot10^{-2}$ | [40] |
| | Ascorbate dianion | 7.2–8.1 | 0.3 | $1.2\cdot10^2$ | [40] |
| Ferredoxin | $PV^+$ | [illegible] | 0.05 | $1.2\cdot10^5$ | [26] |
| Flavodoxin | $MV^+$ | 8.0 | 0.055 | $2.4\cdot10^8$ | [37] |
| Flavodoxin semiquinone | $MV^+$ | 8.0 | 0.055 | $7.0\cdot10^8$ | [37] |

Notation: $MV^+$, $BV^+$, and $PV^+$ are respectively the radical-cations of methylviologen, benzylviologen, and propylviologen; $C_2H_5OH^{\cdot}$ = ethanol radical.

*At 20 °C.

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

The study of the reduction of the acetylated, succinylated, and carboxymethylated cytochrome *c* by solvated electrons and other reductants made it possible to elucidate the role of the electrostatic interaction and of the conformational changes in the redox reactions.[41] It was found that the rate of the reaction involving cytochrome *c* is determined mainly by the conformational change, while electron transfer proceeds in the region of the haem group.

## 2. Quantitative Characteristics of Electron Transfer

The results of studies on the redox reactions of electron transfer agents have been used in the investigation of the possibility of applying outer-sphere transfer theory to protein systems. According to Marcus's ideas,[43] the rate constant for outer-sphere electron transfer $k_{12}$ is related to the reaction equilibrium constant $K$ and the internal exchange rate constants $k_{11}$ and $k_{22}$ for each reactant by the following equation:

$$k_{12}^{\infty} = (k_{11}^{\infty} k_{22}^{\infty} K f)^{1/4},$$

where $\lg f = (\lg K)^2 / 4 \lg (k_{11}^{\infty}/k_{12}^{\infty}/P^2)$ and $P \cong 10^{11}$ litre$^{-1}$ mol$^{-1}$ s$^{-1}$. The above quantity is usually close to unity when $K$ is small. It follows from this equation that the rate of electron transfer depends on the accessibility of the central atom of the complex to individual reactants and also on the difference between the potentials of the reacting compounds, i.e. on the equilibrium constant of the process. If electron transfer at the protein active centre proceeds in the same way as in low-molecular-weight redox compounds, then the internal exchange rate constants for the proteins, calculated for reactions with different reactants, should be identical within the limits of an order of magnitude. Under the conditions of kinetic selectivity, the constants differ by several orders of magnitude.

The study of the rate of reduction of cytochrome *c* by iron complexes containing EDTA derivatives as ligands revealed a satisfactory agreement between the experimental rates and the rates calculated in accordance with outer-sphere transfer theory.[44] A difference is observed only for coordination compounds with an incomplete coordination sphere, which may be due to the increase in the size of the complex owing to the formation of a hydrogen bond between the solvent and a hydroxyl incorporated in this sphere. In the oxidation of cytochrome *c* by substituted ferricenium ions, whose redox potentials ranged over 0.56 V, the calculated and experimental constants were also found to be similar.[45] The enthalpy of activation for the process reaches ~20 kJ mol$^{-1}$ and the entropy varies between −24 and −48 J mol$^{-1}$ K$^{-1}$. These data show that the process does indeed proceed via the formation of a simple bimolecular collision complex without appreciable structural changes in the protein globule.

When coordination compounds of other metals are used instead of isotypical iron complexes, an appreciable scatter of the calculated internal exchange rate constants is observed (Table 3). These constants are almost independent of the nature of the reactant only for two proteins—stellacyanin and rubredoxin. For the remaining proteins investigated, they can differ by more than five orders of magnitude when different reactants are used.

Anomalously high constants are observed in those cases where the interaction between the reactants leads to the formation of complexes, for example the complexes of cytochrome *f* with plastocyanin or cytochrome $c_{551}$ with azurin. Higher and lower constants correspond respectively to reactants incorporating aromatic and hydrophilic ligands, which is associated with the ability of the former to penetrate the hydrophobic region of the active centre. Available data show that iron derivatives containing ethylenediaminetetraacetic acid or its analogues as ligands do not penetrate the protein globule. The constants obtained for these compounds can therefore be used as "reference" values in comparing the reactivities of different proteins. Evidently (Table 3) the internal exchange rate constants obtained using $Fe(EDTA)^{2-}$ are similar for different cytochromes. Stellacyanin and methaemoglobin have the highest and lowest internal exchange rate constants respectively.

In order to eliminate effects associated with the hydrophilic or hydrophobic properties of ligands, an electronically excited ruthenium complex was used (Table 1). Since the

excitation entails a marked increase of the oxidation-reduction capacity of the reactant, this is equivalent to an increase of the driving force of the reaction. The rate constants for bimolecular oxidation-reduction reactions of reduced copper-containing proteins agree well with the theoretical values calculated from the redox potential of the excited complex. This is an important confirmation of the applicability of the outer-sphere electron transfer theory to these metalloproteins. The possibility of applying this theory has been postulated also for other proteins, in particular for flavodoxin.[47]

**Table 3.** The internal exchange rate constants for metalloproteins at pH 7.0 and at 25 °C.

| Protein | Reagent | $k_{11}^{\infty}$, litre mol$^{-1}$ s$^{-1}$ | Refs. |
|---|---|---|---|
| Cytochrome $c_{551}$ | $Co(phen)_3^{3+}$ | $2.2 \cdot 10^5$ | [15] |
| ditto | Stellacyanin | $6.0 \cdot 10^3$* | [46] |
| " | $Co(ox)_3^{3-}$ | 1.4** | [9] |
| " | $Fe(pic)_3^{2-}$ | $4.5 \cdot 10^{-1}$ | [14] |
| " | $Fe(EDTA)^{2-}$ | 2.0 | [14] |
| " | $Co(pic)_2^{-}$ | $2.9 \cdot 10^3$ | [14] |
| Cytochrome *c* | $Fe(EDTA)^{2-}$ | $1.2 \cdot 10^1$ | [15] |
| ditto | $Ru(NH_3)_6^{2+}$ | $1.6 \cdot 10^1$ | [7] |
| " | $Co(phen)_3^{3+}$ | $7.1 \cdot 10^2$ | [7] |
| " | $Ru(NH_3)_5(pyr)^{3+}$ | $2.0 \cdot 10^4$ | [7] |
| " | Ferrocenium ions | $(0.5 - 7.0) \cdot 10^3$ | [45] |
| " | $Co(ox)_3^{3-}$ | 4.6·10$^{1}$** | [9] |
| Cytochrome $b_5$ | $Fe(EDTA)^{2-}$ | 4.3 | [19] |
| Stellacyanin | $Co(ox)_3^{3-}$ | $2.5 \cdot 10^{4}$** | [9] |
| ditto | $Fe(EDTA)^{2-}$ | $2.3 \cdot 10^5$ | [7] |
| " | Cytochrome $c_{551}$ | $2.9 \cdot 10^{4}$* | [46] |
| " | $Ru(NH_3)_5(pyr)^{3+}$ | $1.7 \cdot 10^5$ | [7] |
| " | $Co(phen)_3^{3+}$ | $3.0 \cdot 10^5$ | [7] |
| Plastocyanin | ditto | $1.1 \cdot 10^4$ | [10] |
| ditto | $Fe(EDTA)^{2-}$ | $7.3 \cdot 10^1$ | [10] |
| " | $Ru(NH_3)_4(pyr)^{2+}$ | $4.9 \cdot 10^4$ | [10] |
| " | Cytochrome *f* | $4.0 \cdot 10^{1}$* | [11] |
| Azurin | $Co(ox)_3^{3-}$ | $2.7 \cdot 10^{-3}$** | [9] |
| ditto | $Fe(EDTA)^{2-}$ | $2.8 \cdot 10^{-2}$ | [15] |
| " | $Co(phen)_3^{3+}$ | $1.6 \cdot 10^1$ | [14] |
| " | Cytochrome $c_{551}$ | $8.0 \cdot 10^{2}$* | [11] |
| HPIP | $Co(phen)_3^{3+}$ | $1.8 \cdot 10^4$ | [15] |
| ditto | $Fe(CN)_6^{3-}$ | $1.0 \cdot 10^{1}$* | [23] |
| " | $Fe(EDTA)^{2-}$ | $1.5 \cdot 10^{-2}$ | [15] |
| " | $Co(ox)_3^{3-}$ | $1.1 \cdot 10^{-3}$** | [23] |
| " | $Ru(NH_3)(pyr)^{3+}$ | $2.1 \cdot 10^3$ | [7] |
| | $Ru(NH_3)(pyr)_5^{2+}$ | 2.0 | [15] |
| Rubredoxin | $Ru(NH_3)_6^{2+}$ | $1.0 \cdot 10^{0}$* | [25] |
| ditto | $V(H_2O)_6^{2+}$ | $1.7 \cdot 10^{0}$* | [25] |
| Methaemoglobin | $Fe(EDTA)^{2-}$ | $2.8 \cdot 10^{-3}$ | [24] |
| Metmyoglobin | ditto | $1.3 \cdot 10^{-1}$ | [24] |

*$\mu$ = 0.1 M. **$\mu$ = 0.5 M.

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

The relations arising from the outer-sphere transfer theory have been observed also when organic reactants were employed. Thus for cytochrome *c* or cytochrome *f* a linear dependence of the logarithm of the rate constant on the standard potentials of quinones has been observed experimentally with the slope of the resulting linear plot close to the theoretical value.[48] These experimental data show that the rate-limiting stage of the process is a one-electron transfer and that the internal exchange rate constants for the quinones employed do not differ greatly.

In the reactions of electron transferring proteins with organic reactants, the rate of electron transfer was found to approach a limiting value with increase of the free energy of reaction.[49] This is apparently due to the fact that the energy of the reorganisation of the solvent in these processes is lower than in reactions with inorganic charged complexes and the system approaches the "inversion" region,[43] in which the rate diminishes with increase of the free energy of reaction. It is essential to note that the attainment of a limiting rate for a large free energy change has been observed also in reactions involving low-molecular-weight compounds. In order to account for the experimental data, an empirical expression has been put forward[50] for the free energy of activation, which is equal to the free energy of reaction when the reaction is highly exothermic. This expression has been justified theoretically by Scandola and Balzani.[51]

Together with outer-sphere electron transfer theory, the thermally activated tunnel transfer theory has been used to calculate the rate of the process in proteins.[52–54] According to Chien,[55] the tunnel electron transfer rate constant is given by

$$k_1^{\infty} = 0.6023 \cdot k_{\mu} (2\pi\lambda_0^3 r / R_1)$$

$$k_{\mu} = (4\pi^2/h) |T(r)|^2 (4\pi k_B T\Delta)^{-1/2} \exp[-(E_a - E_b - \Delta)^2/4 k_B T\Delta],$$

$$|T(r)| = 2.7 (N_a N_b)^{-1/2} \exp(-7.2\, r),$$

where $\lambda_0$ is the decay constant, $r$ the electron transfer distance, $R_1$ the radius of the protein molecule, $h$ Planck's constant, $k_B$ Boltzmann's constant, $T$ the absolute temperature, $\Delta$ the vibrational synchronisation parameter, $E_a$ and $E_b$ are the standard potentials of the protein and the mediator, $N_a$ and $N_b$ the numbers of distribution sites for the initial and final wave functions, and $T(r)$ is the electron exchange matrix element. The decay constant for protein molecules is usually assumed to be 0.07 nm and the vibrational synchronisation parameter does not exceed 1 eV.

According to the tunnel transfer theory, the enthalpy and entropy of activation are expressed by the equations

$$\Delta H^{\neq} = (E_a - E_b - \Delta)^2/4\Delta - 3RT/2,$$

$$\Delta S^{\neq} = R \ln \left[ \frac{23.8}{k_B T} \left( \frac{2\pi\lambda_0^3 r}{R_1} \right) \left( \frac{1}{4\pi k_B T\Delta} \right)^{1/2} |T(r)|^2 \right] - \frac{3R}{2}.$$

These equations are used to calculate the vibrational synchronisation parameters and decay constants.

For cytochrome *c*, the rate constants calculated within the framework of the outer-sphere and tunnel transfer theories are similar.[44] However, when ferredoxin is reduced by vanadium and europium complexes or the methylviologen radical-cation, the mutual exchange rate constants calculated using the outer-sphere transfer theory are smaller by four orders of magnitude than the constants determined experimentally for model compounds. At the same time, the calculation performed within the framework of the tunnel transfer theory yields values close to the experimental data.[26] It is essential to note that the calculated constants are extremely sensitive to the vibrational synchronisation parameter and the decay constant. The latter can be calculated from thermodynamic data, but in most cases their use in subsequent calculations does not lead to a satisfactory agreement with experimental quantities.

Assuming that the decay constant is invariant for different metalloproteins, Mauk and co-workers[15] proposed a semi-empirical formula relating the electron transfer distance to the mutual exchange rate constant:

$$r = 0.62 - 0.035 \ln k_{11}^{\infty}.$$

After being reduced by the van der Waals radius, this distance corresponds to the depth of the active centre, which is 0.34–0.69 for cytochromes, 0.28 for plastocyanin, and 0.56 for azurin, and 0.58 nm for high-potential iron-containing proteins. The active centre of stellacyanin is located on the surface of the globule and for this reason the mutual exchange rate constant for this protein has been used in the derivation of the last equation. Its application to

electron transfer agents which do not contain metals leads to results which are satisfactorily correlated with X-ray diffraction data.[56]

### 3. Experimental Data for Electron Transfer in Protein Complexes and Structural Ideas

The rate constants for reactions in protein complexes assume values in the range $10^3$–$10^7$ litre $mol^{-1}$ $s^{-1}$ (Table 4). The pairs of proteins forming complexes in electron transport chains (cytochrome c oxidase–cytochrome c, cytochrome c–cytochrome $b_5$, plastocyanin–cytochrome f, azurin–cytochrome $c_{551}$, etc.) react much faster than proteins which do not give rise to such complexes. Similar pairs are produced as a result of the electrostatic interaction of the positive and negative charges on the aminoacid residues, which has been established in relation to complexes of cytochrome c with cytochrome $c_1$ and cytochrome c oxidase,[68] of cytochrome $b_5$ with methaemoglobin,[69] and of cytochrome $b_2$ with cytochrome c.[70] The formation of complexes between proteins which are not physiological partners is possible on interaction of sections bearing both unlike and like charges.[57,70] The hydrophobic interaction forces apparently play an important role in such cases.

Table 4. The rate constants for electron transfer between proteins (pH 6.1–7.6).

| Oxidant | Reductant | T, °C | μ, M | k, litre $mol^{-1}$ $s^{-1}$ | Refs. |
|---|---|---|---|---|---|
| Azurin | Cytochrome c | 25 | 0.1 | $6.6\cdot10^3$ | [57] |
| ditto | Cytochrome $c_{551}$ | 25 | 0.1 | $3.0\cdot10^6$ | [58] |
| " | Cytochrome $c_{553}$ | 25 | 0.05 | $(2–0.5)\cdot10^6$ | [59] |
| HPIP | Cytochrome $c_2$ | 20 | 0.02 | $(2.4–1.5)\cdot10^5$ | [47] |
| ditto | Cytochrome c | 20 | 0.02 | $(8.7–2.6)\cdot10^4$ | [46] |
| " | ditto | — | 0.21 | $(12–3.8)\cdot10^4$ | [60] |
| Plastocyanin | Cytochrome f | 25 | 0.1 | $3.6\cdot10^7$ | [61] |
| ditto | Cytochrome $c_{553}$ | 25 | 0.1 | $5.0\cdot10^5$ | [61] |
| " | Cytochrome $c_{551}$ | 25 | 0.1 | $7.5\cdot10^5$ | [61] |
| " | Cytochrome c | 25 | 0.1 | $1.0\cdot10^8$ | [61] |
| " | Cytochrome $c_{553}$ | 25 | 0.05 | $4.0\cdot10^5$ | [59] |
| " | Cytochrome c | 25 | 0.10 | $1.5\cdot10^6$ | [57] |
| Cytochrome c | Cytochrome $c_{553}$ | 25 | 0.05 | $4.0\cdot10^4$ | [59] |
| " | Cytochrome $c_{551}$ | 20 | 0.02 | $4.9\cdot10^4$ | [62] |
| " | Azurin | 25 | 0.05 | $1.6\cdot10^3$ | [59] |
| " | Stellacyanin | 25 | 0.1 | $1.9\cdot10^3$ | [46] |
| " | Cytochrome $b_5$ | 25 | 0.1 | $3.0\cdot10^7$ | [63] |
| " | Flavodoxin semiquinone | 23,5 | 0.18 | $1.3\cdot10^5$ | [64] |
| " | Cytochrome $c_1$ | 10 | 1.02 | $2.4\cdot10^5$ | [65] |
| Cytochrome $c_1$ | Cytochrome c | 10 | 1.02 | $3.3\cdot10^5$ | [65] |
| Cytochrome $c_{551}$ | Stellacyanin | 25 | 0.1 | $1.7\cdot10^6$ | [46] |
| Cytochrome c oxidase | Cytochrome c | 25 | 0.1 | $1.0\cdot10^8$ | [66] |
| ditto | ditto | 8 | 0.05 | $3.5\cdot10^7$ | [67] |

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

The groups involved in the formation of the complexes have been discovered by selective modification. In cytochrome c, the Lys-13, Lys-25, Lys-27, Lys-72, and Lys-79 residues are in the vicinity of haem and interact with the negatively charged Asp-48, Asp-60, Glu-43, Glu-44, and haem propionate in cytochrome $b_5$ in a complementary manner.[63] The carboxy-groups of Asp-112, Glu-114, and Glu-198 participate in the interaction of cytochrome c with cytochrome c oxidase.[71] The electrostatic interaction between the two physiological partners in the cytochrome $b_5$-NADH–cytochrome $b_5$ reductase system takes place between the complementary Glu-47, Glu-48, and Glu-52 residues, haem propionate, and the sixth carboxy-group of cytochrome $b_5$, whose position has not been established.[72] The lysine residues at a distance of 3 nm from the redox centres also participate in the reactions of cytochrome $c_3$ with hydrogenase or ferredoxin.[73]
cytochrome $c_3$ with hydrogenase or ferredoxin.[73]

X-Ray diffraction data for individual proteins made it possible to construct models of the complexes and to put forward a hypothetical electron transfer pathway. In the complex of cytochrome c with cytochrome $b_5$, the prosthetic groups are almost coplanar and the distance between the nearest atoms of the porphyrin ring is 0.85 nm.[74] The structure of the cytochrome c peroxidase–cytochrome c complex has been analysed in greater detail.[75] In this complex the His-13, His-27, His-72, His-86, His-87, Gln-12, and Gln-16 residues of cytochrome c interact with the Asp-79, Asp-216, Asp-37, Asp-37, Asp-34, Asn-87, and Gln-86 residues of the peroxidase. In the complex two haem moieties are parallel, but their planes are separated in the vertical direction by a gap of 0.68 nm. The distance between the iron atoms is 2.46 nm and the minimum distance between the haem moieties is 1.65 nm. It has been assumed[75] that the electron transfer in the complex takes place with migration of the free valence, since it has been suggested[76] that this process proceeds via a tunnel mechanism. The experimental detection of the charge-transfer complex between haem and hexacyanoferrate and also of charge transfer in the cytochrome c–$P_{870}$ complex constitutes an important confirmation of tunnel transfer.[77]

Hypothetical models of the cytochrome $b_5$–methaemoglobin [78] and flavodoxin–cytochrome c complexes have also been constructed.[64] In the complex of cytochrome $b_5$ with methaemoglobin subunits, the negatively charged groups of cytochrome $b_5$ interact with the positively charged groups of methaemoglobin. The haem groups in the complex are arranged in parallel at a distance of 0.7–0.8 nm from one another, while the distance between the iron atoms is 1.6 nm. Since the latter is close to the corresponding distance in the cytochrome c peroxidase–cytochrome c complex, presumably the electron transfer between the haem groups proceeds via tunnelling with active participation of the propionate group of the haem in cytochrome $b_5$.[79]

The Lys-13, Lys-25, Lys-27, and Lys-29 residues of cytochrome c and the Glu-120, Glu-65, Glu-62, and Asp-28 groups in flavodoxin take part in the formation of the flavodoxin–cytochrome c complex.[64] The shortest distance between the sulphide bond of Cys-17 in cytochrome c and the methyl group at C(7) of flavin in flavodoxin is 0.34 nm. The distance between the carbon atoms in the conjugate systems is 0.57 nm. The haem and flavin planes are inclined at an angle of 30°, which ensures a satisfactory overlap of the π orbitals and a high rate of electron transfer within the complex. Analysis of X-ray diffraction data for cytochrome $c_3$ [80] and of kinetic results for cytochrome $cd_1$ [81] confirmed the conclusion that a parallel arrangement of the haem groups is essential in order to ensure a high rate of intramolecular electron transfer.

Experimental rates of electron transfer in protein molecules have been obtained using proteins labelled with ruthenium pentammine.[82–84] It has been found that the rates of electron transfer in cytochrome c 20 and 82 $s^{-1}$ over distances of 1.4 and 1.6 nm respectively. In the azurin molecule the electron transfer to the active centre at a distance of 1.2 nm from the label is slower (1.9 $s^{-1}$).[84] An even greater difference between the rates has been observed for electron transfer between the haemoglobin subunits.[85] In this protein the distance between the metal ions is 2.5 nm and the rate of electron transfer is 60 $s^{-1}$. All these results indicate the specificity of the protein globule and the influence of the nature of the active centre. The spatial orientation of both metal atoms and the ligands is extremely

important. Electron transfer between active centres apparently takes place via tunnelling, but one cannot rule out the possibility of valence transfer and also the involvement in this process of intermediate covalent bonds and aromatic aminoacid residues.

## III. QUANTITATIVE CHARACTERISTICS OF THE OXIDATION–REDUCTION REACTIONS OF ENZYMES

Few quantitative data are available for electron transfer with participation of enzymes, which can be accounted for by the high specificity of enzymes and the complexity of the mechanism of their action. Reaction series have been selected for a few enzymes, which made it possible to obtain kinetic data for the redox reactions of catalytically active proteins.

### 1. Oxidation of the Active Centre of Glucose Oxidase

The oxidation of the active centre of glucose oxidase by quinonoid electron acceptors proceeds at rates ranging from $3.5 \times 10^3$ to $1.5 \times 10^6$ litre $mol^{-1}$ $s^{-1}$.[56] The rate of reaction for compounds having the *p*-quinone structure increases with increase of the redox potential of the electron acceptor. There is a linear relation between the logarithms of the rate constants and the potentials of the acceptors, which is described by a correlation straight line with a slope of 8.4 $V^{-1}$.

Inorganic complexes react with reduced glucose oxidase more slowly despite their high potential, but the rate of oxidation by hexacyanoferrate(III) greatly increases in an acid medium. At a high ionic strength of the solution the phenanthroline or bipyridyl complexes of cobalt react with the above substrate at a rate which is close to the rate of its oxidation by hexacyanoferrate(III), but, when the pH is diminished (to 4), the rate changes much less.

The data obtained led to the following conclusions: (1) the rate-limiting stage of the process is one-electron transfer, because the rates of reactions with participation of one-electron acceptors (tetracyano-*p*-quinodimethane and its radical-anion) obey the Brønsted relation; (2) electron transfer takes place via the outer-sphere mechanism; (3) derivatives of *o*-quinones form an independent group of acceptors, which have a higher reactivity than the *para*-derivatives owing to the *ortho*-effect; (4) the low rate of oxidation of glucose oxidase by inorganic compounds is caused by the specificity of the action of one-electron acceptors, which is determined by the presence of the charge.

The mutual exchange rate constants for glucose oxidase calculated on the basis of the outer-sphere transfer theory are $10^{-2}$–$10^{-9}$ litre $mol^{-1}$ $s^{-1}$ at a high ionic strength and the electron transfer distance for inorganic reagents is 1.1 to 1.3 nm in a neutral medium and 0.8–0.9 nm in the acid region. In the case of hydroquinone the distance is 0.88 nm. These differences in the calculated distances are determined by the degree of penetration of the reagents into the active centre zone, which entails structural changes in the protein globule.

### 2. Reactions of Cytochrome $b_2$ with Electron Acceptors

The rate constants for the oxidation of cytochrome $b_2$ by organic electron acceptors depend on the redox potentials of the compounds and vary in the range $1.2 \times 10^4$–$4.7 \times 10^7$ litre $mol^{-1}$ $s^{-1}$.[86] A linear relation is observed between the logarithm of the rate constant and the redox potential, the slope of the corresponding plot being 8.6 $V^{-1}$. Reduced cytochrome $b_1$ also reacts with inorganic complexes, haem being oxidised, while organic electron acceptors interact with another prosthetic group of the enzyme (FMN). The rate constants for mutual exchange with the complexes, calculated from kinetic data, vary in the range $1 \times 10^1$ to $6.6 \times 10^6$ litre $mol^{-1}$ $s^{-1}$, while the constant for *p*-benzoquinone is $1.6 \times 10^3$ litre $mol^{-1}$ $s^{-1}$. This constant is particularly large for the bipyridyl complex of cobalt, which reacts in the cytochrome *c* binding zone. The electron transfer distance for non-penetrating complexes is 0.31–0.54 nm, while for *p*-benzoquinone it is 0.36 nm. These values agree with those obtained for other cytochromes.

### 3, Characteristics of Electron Transfer in the Peroxidase Process

The formation of active intermediate states of the enzyme (the complexes $E_1$ and $E_2$) is characteristic of the catalysis by peroxidase.[87] It has been suggested that the iron in compound $E_2$ is in the ferryl [$FeO^{2+}$] state. In $E_1$ one of the oxidation equivalents exists in the form of the porphyrin $\pi$-radical-cation, while the other is analogous to the $E_2$ equivalent. In cytochrome *c* peroxidase the free radical is localised at the Trp-51 residue and not on the porphyrin ring.[88] The oxidation-reduction potentials of the two forms of enzymes depend little on the pH and amount to 0.963 V for the $E_2/E$ transition and 0.94 V for the $E_1/E_2$ transition.[87]

Table 5. The rate constants for the reduction of peroxidases at 25 °C.[89–92]

| Peroxidase | Reagent* | pH | $\mu$, M | $k_{12}$, litre $mol^{-1}$ $s^{-1}$ |
|---|---|---|---|---|
| Cytochrome *c* peroxidase ($E_2$ complex) | $Co(tpyr)_2^{2+}$ | 7.0 | 0.1 | $1.1 \cdot 10^5$ |
| ditto | $Ru(NH_3)_5(pyr)^{2+}$ | 7.0 | 0.1 | $9.5 \cdot 10^5$ |
| " | $Fe(CN)_6^{4-}$ | 7.0 | 0.1 | $7.6 \cdot 10^3$ |
| " | $Fe(CN)_6^{4-}$ | 5.26 | 0.1 | $8.1 \cdot 10^3$ |
| " | $Fe(bpyr)_3^{2+}$ | 5.26 | 0.1 | $3.6 \cdot 10^5$ |
| " | $Fe(dmbpyr)_3^{2+}$ | 5.26 | 0.5* | $4.2 \cdot 10^5$ |
| " | $Fe(tmbpyr)_3^{2+}$ | 5.26 | 1.0 | $1.2 \cdot 10^4$ |
| " | $Fe(phen)_2(CN)_2$ | 5.26 | 2.0 | $3.4 \cdot 10^4$ |
| " | $Fe(phen)(CN)_4^{2-}$ | 5.26 | 1.0 | $8.0 \cdot 10^5$ |
| Horseradish peroxidase ($E_1$ complex) | $Fe(CN)_6^{4-}$ | 6.93 | 0.11 | $8.5 \cdot 10^5$ |
| Horseradish peroxidase ($E_2$ complex) | $Fe(CN)_6^{4-}$ | 6.83 | 0.11 | $1.8 \cdot 10^4$ |
| Horseradish peroxidase | $Co(sep)^{2+}$ | 6.3 | 0.15 | $7.0 \cdot 10^4$ |
| ditto | | 6.3 | 0.15 | $5.0 \cdot 10^5$ |
| " | $MV^+$ | 7.0 | $\infty$ | $4.9 \cdot 10^5$ |

Notation: tpyr = terpyridyl; dmbpyr = dimethylbipyridyl; tmbpyr = trimethylbipyridyl.

*At 20 °C.

The reduction of the complex $E_1$ by inorganic compounds proceeds in most cases via a one-electron mechanism with formation of the complex $E_2$. The rate constants for the reduction of the complex $E_1$ are in the range $10^4$–$10^7$ litre $mol^{-1}$ $s^{-1}$ (Table 5). Ruthenium derivatives containing an aromatic compound as the ligand reacts at an exceptionally high rate.[89] Ferriperoxidase is also reduced by powerful reductants to the ferro-form. The standard potential of this transition is −0.25 V.[93] Cobalt sepulchrate, whose

standard potential is −0.3 V, reacts at a rate of $7 \times 10^4$ litre $mol^{-1}$ $s^{-1}$, while dithionite reacts faster almost by an order of magnitude.[92] In the reactions of ferriperoxidase with $MV^+$, a marked dependence of the rate of reduction on the ionic strength of the solution is observed. The charge of peroxidase calculated from these results is −5. It has been shown[90] that, in the reduction of cytochrome *c* peroxidase in the $E_2$ state by iron complexes, a linear relation is observed between the free energies of reaction and activation, which agrees with the outer sphere transfer theory. The mutual exchange rate constant calculated for hexacyanoferrate(II) is $7.5 \times 10^{-5}$ litre $mol^{-1}$ $s^{-1}$ while that calculated for the bis-(terpyridyl)cobalt(II) is $1.3 \times 10^{-4}$ litre $mol^{-1}$ $s^{-1}$. The mutual exchange rate constant for the complex $E_2$ of horseradish peroxidase is almost an order of magnitude smaller ($9 \times 10^{-7}$ litre $mol^{-1}$ $s^{-1}$) when hexacyanoferrate(II) is used. The electron transfer distances calculated from these data are 0.93, 0.95, and 1.1 nm respectively for the above three cases.

The free energies of the reactions of ferriperoxidase with reductants are smaller than for the reactions involving the complexes $E_1$ or $E_2$ and the probability that the system enters the inversion region diminishes. The present authors determined[4] the mutual exchange rate constant for the interaction of $MV^+$ with ferriperoxidase. It amounts to 3.6 litre $mol^{-1}$ $s^{-1}$ and the electron transfer distance is 0.58 nm. Calculation within the framework of tunnel transfer with $\Delta = 0.8$ eV and a decay constant of 0.07 nm, adopted by analogy with ferricytochrome *c*, also yielded an electron transfer distance of 0.58 nm.

### 4. The Oxidation of Electron Donors in the Laccase Reaction

Laccase is one of the few oxidases which reduce molecular oxygen to water in a four-electron process. The active centre of laccase includes copper ions of three types which are in the bivalent state and all participate in the catalytic reduction of oxygen. Laccase is a two-substrate enzyme catalysing the oxidation of the hydroxy-derivatives of benzene or inorganic ions by molecular oxygen. The rate constant for the bimolecular interaction of the laccase active centre with oxygen is $1.6 \times 10^6$ litre $mol^{-1}$ $s^{-1}$ and the rates of oxidation of substrates vary in the range $1.0 \times 10^5$–$2.5 \times 10^6$ litre $mol^{-1}$ $s^{-1}$ and depend on the nature of the enzyme.[94,95] The rate constants for the reduction of the active centre are not correlated with the redox potentials of the donors. However, for one of the laccases investigated,[95] an increased bimolecular constant has been observed for a series of hydroquinones containing substituents with an unshared electron pair despite the fact that the introduction of the substituent increases the redox potential of the electron donor. A similar effect of substituents has likewise been observed in the study of prestationary kinetics of the reduction of copper of the first type in laccase.[96] It has been suggested that this is caused by the additional coordination of the nucleophilic substituent to copper atoms of the third type. This in fact accounts for the appreciable increase of the constant for the inhibition by the fluoride ion of the oxidation of 2,3-dicyanohydroquinone, because the affinity of fluoride for copper of the second type also diminishes on coordination of copper of the third type to the azide.[97]

Kinetic data for the reduction of the active centre of laccase by hydroquinone and hexacyanoferrate(II), obtained by the stopped flow method,[98] permit the conclusion that the reaction proceeds via the outer sphere transfer mechanism. The absence of the Brønsted relation in oxygen reduction processes is due to the complexity of the mechanism and the four-electron reduction of oxygen.[98]

An important question in catalysis by laccase is that of the nature of the high potential of the active centre of the enzyme. Spectroelectrochemical measurements of the redox potential of laccase in the range 7–41 °C yielded the following changes in the thermodynamic parameters and the reduction potential of the active centre: $\Delta S = -58.2$ J $mol^{-1}$ $K^{-1}$, $\Delta H = -92.6$ kJ $mol^{-1}$, and $E$ (25 °C) = 780 mV.[99] Comparison of the entropy and enthalpy parameters with the values known for one-centre metalloproteins permits the conclusion that the high potential of the blue copper is due mainly to stabilisation by ligands, while protein solvation effects play an appreciably smaller role.

## IV. THE RATES OF ELECTROCHEMICAL REACTIONS OF PROTEINS

There exists a profound analogy between electron transfer processes in solution and electrode reactions. Within the framework of the simple isotropic medium models, the outer-sphere transfer theory yields the following expression relating the rates of the processes in the bulk of the solution and on the electrode surface:[43]

$$(k_h/P_h)^{1/2} \geqslant k_s/P_s ,$$

where $k_h$ and $k_s$ are the rate constants for the bimolecular and heterogeneous processes respectively and $P_h$ and $P_s$ are the numbers of the maximum possible collisions in the bulk (~$10^{11}$ litre $mol^{-1}$ $s^{-1}$) and on the surface (~$10^4$ cm $s^{-1}$). With the aid of this equation, it is possible to estimate the rates of electrochemical reactions of proteins on the basis of kinetic results, while the concept of tunnel transfer[100] makes it possible to calculate the rate from structural data for protein molecules.

### 1. The Redox Reactions of Proteins at the Mercury Electrode

In the early investigations the electrochemical properties of proteins were most often studied at dropping and stationary mercury electrodes. Cytochrome *c* was the first protein to be investigated and it has been studied in greatest detail.[101] In the numerous investigations devoted to this protein, different degrees of reversibility of the electrochemical reactions of cytochrome *c* at mercury electrodes were observed. For example, Betso et al.[102] and Scheller et al.[103] believe that the reduction of cytochrome c at low concentrations is reversible. However, other investigators[104,105] have shown that, in contrast to haemin, native cytochrome *c* is reduced with a high overpotential, reaching 0.3 V, while the heterogeneous rate constant for this process is extremely low ($10^{-10}$–$10^{-11}$ cm $s^{-1}$). The observed difference in the electrochemical behaviour of cytochrome c is apparently caused by the different compositions of the medium and by the presence of impurities. Indeed it has been shown recently[101] that, even in highly purified protein preparations, there is an admixture which influences significantly the rate of the electrochemical reaction.

The study of electrochemical properties of cytochrome *c* at the mercury electrode made it possible to formulate the problem of the state of the protein globule on its surface. It has been suggested that the first adsorbed portions of the protein "are flattened" and are irreversibly denatured on the electrode surface.[106,107] According to Kuznetsov,[108] the cytochrome c molecules are discharged within the pores of the monolayer. The adsorption of native globules in such

pores is reversible. The area of the pore is 4 $nm^2$ for cytochrome *c*, which is smaller by a factor of 2.25 than the cross-sectional area of the native protein molecule. It is essential to note that the adsorption of cytochrome *c* on the second and subsequent layers is slower compared with the adsorption on the free mercury surface. For this reason, at a high overpotential, electron transfer may be limited by the exchange of the adsorbed and freely diffusing molecules. As a result, the limiting currents do not reach the values obtained from the Ilkovič equation.

Cytochrome $c_7$, whose structure resembles that of cytochrome *c*, is a three-haem protein. This low-potential haemoprotein is reduced reversibly at −0.17 and −0.22 V.[109] The rate of the process is determined by diffusion and electron transfer not retarded by the adsorption of the protein. Another cytochrome, namely cytochrome $c_{553}$, has a low molecular weight, but its haem environment differs from that in cytochrome *c*. The electrochemical reaction of cytochrome $c_{553}$ is quasi-reversible.[110] The cathodic reduction overpotential of this cytochrome does not exceed 40 mV and the redox potential of the system is 0.02 V. The electrochemical reduction of the four-haem cytochrome $c_3$ is reversible with a low rate constant (>0.1 cm $s^{-1}$) but takes place stepwise owing to the non-equivalence of the haem groups in the protein molecule.[111,112]

Cytochrome $b_5$ partly cleaved by trypsin gives rise to distinct waves under the conditions of classical polarography and the half-wave potential is near its redox potential.[113] The native cytochrome $b_5$, isolated using detergents, is reduced at the mercury electrode with much more difficulty and a much higher overpotential, while cytochrome P-450 is not reduced at all.[113] Other haem-containing proteins, whose natural functions consist in electron transfer, namely metmyoglobin and methaemoglobin, are reduced at the electrode with a high overpotential and irreversibility.[114,115]

Comparison of the electrochemical properties of haem-containing electron transferring proteins shows that only low-molecular proteins with low redox potentials, which are correlated with the degree of accessibility of haem to water, undergo rapid electrochemical reactions.[116] Consequently the structural features of the protein molecule play an appreciable role in electrochemical reactions. There is no doubt that the adsorption and orientation factors also affect the rate of the process. The weak adsorption and (or) aggregation of cytochrome $b_5$ is apparently the cause of the slowness of the reaction, although the active centre has an appreciable area of contact with the aqueous medium.

The electrochemical properties of other proteins have also been investigated at the mercury electrode. The reduction of ferredoxin from higher plants takes place at −0.33 V and that of bacterial ferredoxin occurs at −0.325 V and protons participate in the electrode reaction.[117] The available literature data show that ferredoxins of plant and microbial origin behave differently at the electrode.[118]

Comparative electrochemical studies of five proteins, namely ferredoxin, rubredoxin, flavodoxin, cytochrome $c_3$, and cytochrome *c*, have revealed the following features:[119]

(1) The positively charged cytochrome $c_3$ is reduced readily at the mercury electrode, because the process takes place below the zero-charge potential of mercury, and poly-L-lysine inhibits the process.

(2) Bacterial and plant ferredoxins as well as flavodoxin are negatively charged. Their redox potentials are identical with the zero-charge potential of the electrode. For this reason, a high rate of electrochemical reaction is observed only in the presence of positively charged surfactants.

(3) The positively charged cytochrome c is slowly reduced on the positively charged electrode in the region of the redox reaction of the protein.

All these factors permit the conclusion that electrostatic interaction plays a significant role in the electrochemical reactions of proteins and that the reduction of positively charged proteins is slow at a positive potential higher than the zero-change potential. Similar difficulties arise also in the reduction of negatively charged proteins if the electrode potential is more negative than the charge of the protein [the electrode potential corresponds to a charge more negative than that of the protein?]. A non-uniform distribution of charges on the surfaces of the protein globules can, however, lead to the observation of the effective interaction of like charges on the electrode and the protein or, conversely, the process may not occur despite the fact that they have opposite charges. An example is provided by data for the reduction of the negatively charged rubredoxin and flavodoxin, whose redox reactions do not occur when the mercury electrode is positively charged.[119] Therefore, as in cytochrome *c*, the orientation of the dipole in these proteins is such that it forms an angle with the haem group. Consequently, as the protein molecule approaches the positively charged surface, the side groups interact preferentially and the active centre does not come into direct contact with the electrode.

The electrochemical reduction of enzymes whose molecular weight is higher than that of the electron-transferring proteins proceeds as a rule with dissociation of the co-factor.[114] Even in the case of cholesterol oxidase, in which FAD is bound to the protein by a covalent bond, adsorption leads to the partial liberation of the cofactor and the electrochemical properties of the system are determined by the redox reactions of FAD in the presence of the denatured protein.[120] The catalytically active fragments of glucose oxidase are formed on partial cleavage of the native structure of the enzyme and are reduced at a potential higher by 0.1 V than the reduction potential of FAD.[121] Furthermore, the enzymically reduced enzyme is oxidised electrochemically with a low overpotential. The agreement of the half-wave potential $E_{1/2}$ with the redox potential of the enzyme and the constancy of $E_{1/2}$ as the enzyme concentration is varied show that the glucose oxidase fragment reacts reversibly. Native glucose oxidase reacts quasi-reversibly on platinum electrodes.[122]

Other proteins investigated, including flavoproteins from egg yolk, are denatured when adsorbed on the mercury electrode with liberation of the co-factor, which is reduced in the region of the redox potential.[121] When peroxidase is adsorbed on an amalgamated gold electrode, an oxidation-reduction process is observed, but it is associated with redox reactions of the disulphide bonds.[123]

### 2. Electrochemical Reactions of Proteins on Solid Electrodes

It was shown in early investigations that the electrochemical reaction of cytochrome *c* on gold, platinum, nickel, silver, and other metallic electrodes and on the silicon *p*-type semiconductor electrode is irreversible.[101] A quasi-reversible reaction of cytochrome *c* has been observed on optically transparent electrodes.[124] It has been shown[101] that thoroughly purified cytochrome *c* reacts quasi-reversibly on a tin-doped indium oxide electrode with a heterogeneous rate constant of $4.9 \times 10^{-3}$ cm $s^{-1}$. Detailed investigation of the electrochemical reaction of cytochrome *c* on solid electrodes showed that the rate of the process depends not only on the degree of purification of the protein but also on the method used to prepare the electrode and on the composition of the buffer solution.[125] The available data demonstrate convincingly that cytochrome *c* can exchange electrons with

various electrodes. The rate of the process is then close to that calculated from the mutual exchange rate constant, which amounts to 0.1 cm $s^{-1}$ when account is taken of the steric factor (0.025).[126]

The reduction and oxidation of ferredoxin on pyrolytic graphite electrodes proceeds reversibly only in the presence of magnesium ions.[127,128] The electrochemical reactions of rubredoxin, flavodoxin, and ferredoxin on the same electrodes in the presence of positively charged chromium hexammine ions or magnesium ions are either quasi-reversible or reversible.[129] Ions are not required for the rapid reaction of azurin. The observed phenomena can be accounted for by the fact that all the proteins investigated are negatively charged and have redox potentials in the region of which the graphite surface has a negative capacitive charge. The positively charged ions are concentrated in the outer plane of the Helmholtz layer and thereby diminish the repelling effect of the electrode on rubredoxin, flavodoxin, and ferredoxin. The weak influence of the positively charged ions in the case of azurin is caused by the high degree of charge pairing between side groups.

The electrochemical oxidation of cytochrome $b_5$ at platinum gauze electrodes takes place at 0.9 V, while the reduction of the enzyme is masked by the reduction of water.[130] The data obtained indicate the irreversibility of the electrochemical reaction of the enzyme. However, spectroelectrochemical studies have shown that both cofactors (FMN and haem) exchange electrons via an independent pathway.

The electrochemical reactions of oxygen transporting agents are extremely low. It has been shown[4] that the electrochemical reaction of methaemoglobin at the $SnO_2$ electrode proceeds irreversibly with a heterogeneous constant of $5.2 \times 10^{-8}$ cm $s^{-1}$ and a transport coefficient of 0.29. The adsorption of the tetraethylammonium ion increases the constant by a factor of 3. This may be caused by the change in the potential of the diffuse layer of the electrode following the adsorption of the surface-active cation.

### 3. The Oxidation-Reduction Reactions of Proteins on Modified Electrodes

The results for the electrochemical reactions of proteins on solid electrodes discussed above show that the rate of the process is greatly influenced by the state of the electrode–buffer solution interface. Modifying agents are used to alter it in a specific manner (Table 6). The electrochemical reactions of cytochromes on gold, carbon, or platinum electrodes modified with 4,4′-bipyridyl or its sulphur-containing analogues take place at the equilibrium potential with a high rate constant, which is close to the constant for the thoroughly investigated hexacyanoferrate(III)/hexacyanoferrate(II) pair. Together with these four analogues of 4,4′-bipyridyl, several compounds capable of accelerating the redox reaction of cytochrome *c* are known: 4,4′-azopyridyl, 2,5-di(4-pyridyl)-1,3,4-thiadiazole, and purine and its derivatives.[133,145] The modifying agents each contain as a rule one nitrogen atom at the ends of the molecule, have a definite length, and possess a conjugated electron system. Other compounds which do not meet these requirements but whose structure is close to that of 4,4′-bipyridyl, such as pyridine, pyrazine, 4-phenylpyridine, 2,2′-bipyridyl, and 1,2-di(4-pyridyl)ethane, do not increase the electrochemical activity of cytochromes.

The mechanism of the action of the modifying agents consists in their adsorption on the electrode surface and the formation of a layer on which proteins are absorbed.[146] Positively charged lysine residues participate in the interaction of the protein with the adsorption layer, which promotes the orientation of haem towards the electrode surface.

The mechanism of the action of another modifying agent, polyethyleneimine, apparently also consists in orienting the protein globules.[134] However, the concentration dependence of the potential of the redox reaction of the protein and the dependence of the reaction current on the electrode modification time have shown that polyethyleneimine does not form a continuous coating on the electrode.

Table 6. Electrochemical parameters of proteins determined on chemically modified electrodes.

| Protein | Electrode | Modifying agent | Electrochemical parameters | | Refs. |
|---|---|---|---|---|---|
| | | | $k_s$, cm $s^{-1}$ | $\alpha$ | |
| Cytochrome *c* | Au | 4,4′-Bipyridyl; 1,2-di-(4-pyridyl)ethylene | $1.9 \cdot 10^{-2}$ | — | [131] |
| ditto | Au | di(4-pyridyl) disulphide; di(4-pyridyl) sulphide | $(2.1—8.9) \cdot 10^{-3}$ | — | [132] |
| » | Au | Purine | $1.0 \cdot 10^{-3}$ | — | [133] |
| » | $SnO_2$ | Polyethyleneimide | — | 0.3 | [134] |
| » | C | 4,4′-Bipyridyl | $4.4 \cdot 10^{-4}$ | — | [135] |
| Cytochrome $c_3$ | Au | ditto | $>10^{-2}$ | — | [131] |
| Cytochrome $c\,d_1$ | C | » | $4.0 \cdot 10^{-4}$ | | [135] |
| Cytochrome *c* | Au | Methylviologen | $3.4 \cdot 10^{-5}$ | 0.25 | [136] |
| Myoglobin | Au | ditto | $7.7 \cdot 10^{-5}$ | 0.18 | [136] |
| ditto | Au | » | $3.9 \cdot 10^{-11}$ | 0.18 | [137] |
| Ferredoxin | Au | » | $(59—6.5) \cdot 10^{-5}$ | 0.4—0.6 | [138,139] |
| Peroxidase | Au | *NN*′-Di(2-aminoethyl)bipyridyl; methylviologen; benzylviologen | $(84—1.3) \cdot 10^{-5}$ | 0.31—0.71 | [140] |
| Cytochrome *c* | Au, Pt | *NN*′-Bis[3](trimethoxysilyl)propyl] bipyridyl | $<0.06$ | — | [141] |
| ditto | C | *N*-Vinyl-4,4′-bipyridyl | — | — | [142] |
| » | Pt | Polyalkylated ferrocene | $(2.4—8.7) \cdot 10^{-4}$ | — | [143] |
| » | *n*-Si | | $(1.8—3.5) \cdot 10^{-4}$ | — | [144] |
| Ferredoxin | C | *NN*′-Di(3-aminopropyl)-bipyridyl | $(1.6—4.0) \cdot 10^{-3}$* $>10^{-2}$** | — | [145] |

*For bacterial ferredoxin. **For plant ferredoxin.

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

Viologens polymerised on gold electrodes are also used as modifying agents.[136–140] The constants for the electrochemical reactions of proteins on such electrodes are, however, small and the transfer coefficient $\alpha$ in certain systems is close to unity (Table 6). The action of polyviologens as agents promoting the electrochemical reactions of proteins has a mechanism analogous to that of the action of 4,4′-bipyridyl, which has been confirmed by the electrochemical inertness of the modifying agents as regards the redox reactions of proteins. Furthermore, polyviologens are conjugated molecules whose end groups contain nitrogen atoms, so that they resemble bipyridyl.

Electrodes modified with *NN'*-bis[3-(trimethoxysilyl)-propyl]bipyridyl and related compounds (Table 6) contain immobilised viologens or ferrocene. The electrochemical reactions of proteins on these electrodes proceed via a mediator mechanism.[147] For cytochrome *c*, the process can be represented by the following equations:

$$MV^{2+} + e \xrightarrow{k_S} MV^{+},$$

$$MV^{+} + \text{cytochrome } c \text{ (oxidised)} \rightarrow MV^{2+} + \text{cytochrome } c \text{ (reduced)}.$$

The rate constant for the bimolecular reaction in this process exceeds $10^8$ litre $mol^{-1}$ $s^{-1}$. The rate of the process is limited by the reaction of the protein on the electrode surface and the current is therefore directly proportional to the square root of the rate of potential scan.[141,144]

### 4. Electrochemical Reactions of Covalently Immobilised Enzymes

When glucose oxidase is immobilised on graphite electrodes via cyanuric chloride, the differential pulse voltamperogram shows a peak at −0.31 V.[148] The potential of this peak is displaced by 20 mV towards the cathodic region compared with the enzyme adsorbed on the graphite electrode and by 100 mV into the anodic region compared with the redox reaction of the enzyme in solution. Immobilised L-amino-acid oxidase and xanthine oxidase react at the same potentials.[149] These results demonstrate the possibility of direct electron transfer to flavin oxidases. However, the native state of the immobilised enzymes, i.e. their ability to catalyse the reactions of substrates, remains open to doubt. The point is that the enzymes investigated readily dissociate into the apoenzyme and the co-factor. The fact that the proteins are reduced at a potential differing from the reduction potential of the adsorbed FAD does not fully demonstrate the native state of the enzyme, because it can be due to the reduction of the FAD, which is associated [with the protein? (Ed.of Translation)] in a region other than that of the active centre. Such effects are observed, for example, in the association of FAD within an inert protein.[106]

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Thus the electron transfer proteins and oxidation-reduction enzymes react similarly to non-protein redox systems. The specificity of the action of the polypeptide chain consists in regulating the potential of the active centre and its orientation in complexes where electron transfer takes place. One cannot rule out the possibility that the side groups of the aminoacids are directly involved in electron transfer over long distances, as shown for the cytochrome *c* peroxidase–cytochrome *c* complex.[150] Further progress in the study of the mechansim of electron transfer in proteins depends to a large extent on the elucidation of the contribution of the polypeptide chain to the activation energy and the adiabatic nature of the transfer. Extremely interesting results on these lines have been obtained in a number of studies.[151–154]

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# The Synthesis of Prostacyclin and Its Analogues

V.A.Dombrovskii, E.V.Gracheva, and P.M.Kochergin

The advances in the synthesis of prostacyclin and its analogues are examined. The bibliography includes 114 references.

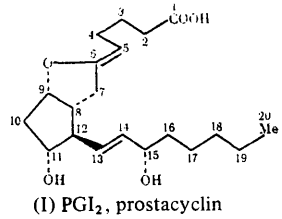
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## I. INTRODUCTION

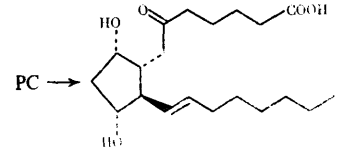
Much attention is being devoted at present to prostacyclin (PC)—a substance which is tens of times more active than any of the prostaglandins (PG). PC is formed from arachidonic acid in minute amounts in the heart and in the walls of the blood vessels. Investigators have assigned a special place to PC because, in contrast to PG, it does not decompose in the lungs and, circulating in the blood, it tends to reduce the arterial pressure. PC has yet another exceptional property—the ability to prevent the development of atherosclerosis and especially its severe consequence—the formation of clots in the blood vessels.[1]

By incubating the endoperoxides $PGG_2$ and $PGH_2$ with the enzyme system of the microsomal fraction of the arterial vessels, Vane and co-workers[2,3] observed in 1976 the formation of an unstable substance which proved to be a powerful inhibitor of the aggregation of platelets. This substance, initially designated by PGX, was subsequently characterised as (5Z)-9-deoxy-6,9α-oxido-$\Delta^5$-$PGF_{1\alpha}$ [4,5] and now bears the trivial name prostacyclin or the abbreviation $PGI_2$ or (I). PC is at the present time the most powerful inhibitor of the aggregation of platelets[6] and possesses strong vasodilating properties.[2,7-9]



(I) $PGI_2$, prostacyclin

The chemistry of PC is determined by characteristic groups, one of which is the vinyl ether group incorporating the C(5)–C(6) atoms and the oxygen atom attached to C(9) in this molecule.[4,5,10] The potential value of PC as a therapeutic agent, particularly when its prolonged action is required, is appreciably reduced owing to the fact that its vinyl ether group is very readily and rapidly hydrolysed (the half-decomposition time is 10 min at pH 7.6 at 25 °C) which leads to the formation of 6-oxo-$PGF_{1\alpha}$.[11,12] The problem therefore arose of the synthesis of chemically stable analogues of PC possessing a high selective activity while retaining, in principle, the structure of PG, since PC, which is ultimately transformed into the usual $PGF_{1\alpha}$ metabolites, reduces the adhesion and sticking together of blood platelets 1000 times more effectively than the stable 6-oxo-$PGF_{1\alpha}$ and 30 times more effectively than $PGE_1$.[2,3] The tactics and strategy used in the synthesis of PG and their analogues, developed between 1960 and 1980,[13-15] helped to solve the problem of the synthesis of PC and its analogues.



6-oxo-$PGF_1$

The growing interest in PC analogues led to the publication of numerous studies on the synthesis and pharmacological properties of these compounds. However, the data on their synthesis have been scarcely treated systematically or surveyed. A monograph[16] and a review[17] are mainly devoted to the pharmacological properties of PC and its analogues and in another review[18] the methods of synthesis of PC and thromoboxanes are examined extremely concisely. We therefore thought it useful to review the most important studies on the synthesis of PC and its analogues.

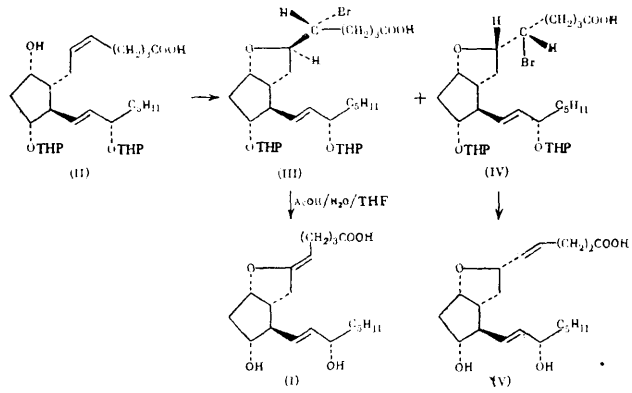
## II. THE SYNTHESIS OF PROSTACYCLIN AND ITS ANALOGUES

### 1. Synthesis from Natural Prostaglandins and Their Analogues

The simplest and most general method of synthesis of PC and its analogues involves the modification of natural PG or their analogues, including the following series of reactions: (1) intermolecular nucleophilic addition of bromine or iodine to the C(5)–C(6) double bond of PG with the simultaneous formation of the ring; (2) elimination of HBr or HI with alkali or reductive elimination of iodine.

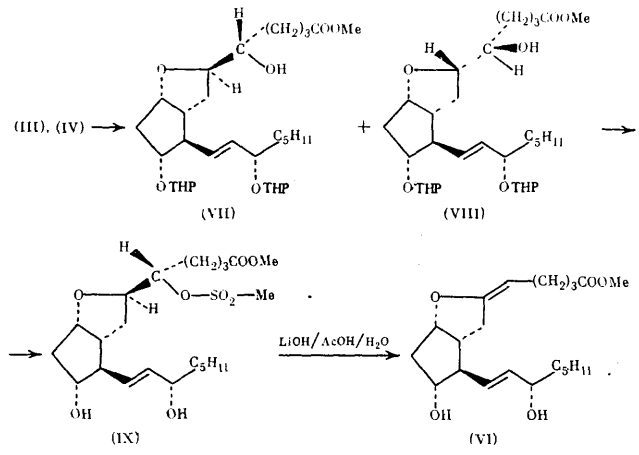
The required stereochemistry of the C(5) atom is retained in all the transformations, since the main processes are the *trans*-addition of the halogen to the double bond and the *trans*-elimination of HBr or HI. For example, the bromination of $PGF_{2\alpha}$ (II) with *N*-bromosuccinimide (NBS) yields a mixture of diastereoisomers of the 5-bromo-substituted $PGI_1$ (III) and (IV) (3 : 1). After the removal of the tetrahydropyranyl (THP) protecting group from the diastereoisomer (III) and the elimination of HBr by treatment with *t*-BuOK/BuOH, PC [compound (I)] is formed. The diastereoisomer (IV), formed as a minor product in the cyclisation stage, gives rise to $\Delta^4$-6α-$PGI_1$ (V) after the same treatment as that described for compound (III) [19,20] (Scheme 1).

Scheme 1

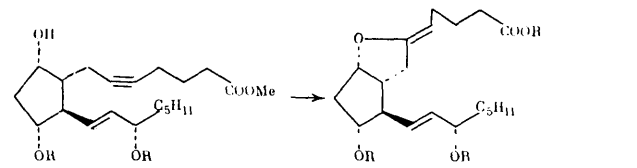


Corey and co-workers described the synthesis of (5*E*)-$PGI_2$ (VI) from the intermediates (III) and (IV),[21] whose treatment with $K_2O$ and 18-crown-6 ether in dimethyl sulphoxide (DMSO) leads to the corresponding mixture of alcohols with inversion at the C(5) atom (85%). The mixture of alcohols is esterfied with diazomethane to compounds (VII) and (VIII), which are then converted into the methanesulphonate (IX) (84%) by reaction with methanesulphonyl chloride and triethylamine. The THP groups in compound (IX) are removed in the usual way and the product is hydrolysed to the corresponding acid, which is then treated with an excess of t-BuOK/BuOH to form compound (VI) (Scheme 2).

Scheme 2



Suzuki[22] proposed a simple stereospecific synthesis of PC, with a small number of stages, starting from the derivative 5,6-dihydro-$PGF_{2\alpha}$. The chiral acetylenic alcohol (X) is converted into the cyclic product (XI). The removal of the protecting groups in compound (XI) by treatment with tetra-n-butyl ammonium fluoride (TBAF) in tetrahydrofuran (THF) affords the methyl ester of $PGI_2$ (XII) (74%), the alkaline hydrolysis of which leads to $PGI_2$ (I).



(X): R = Si(Me)$_2$-t-Bu

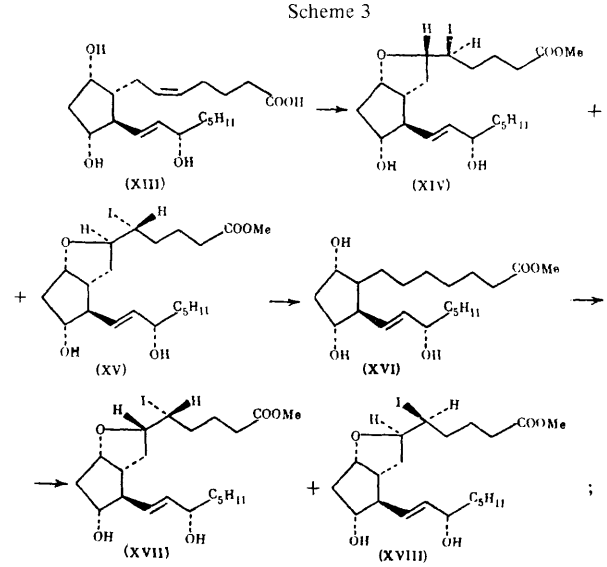
(XI): R = Si(Me)$_2$-t Bu, R$^1$ = Me

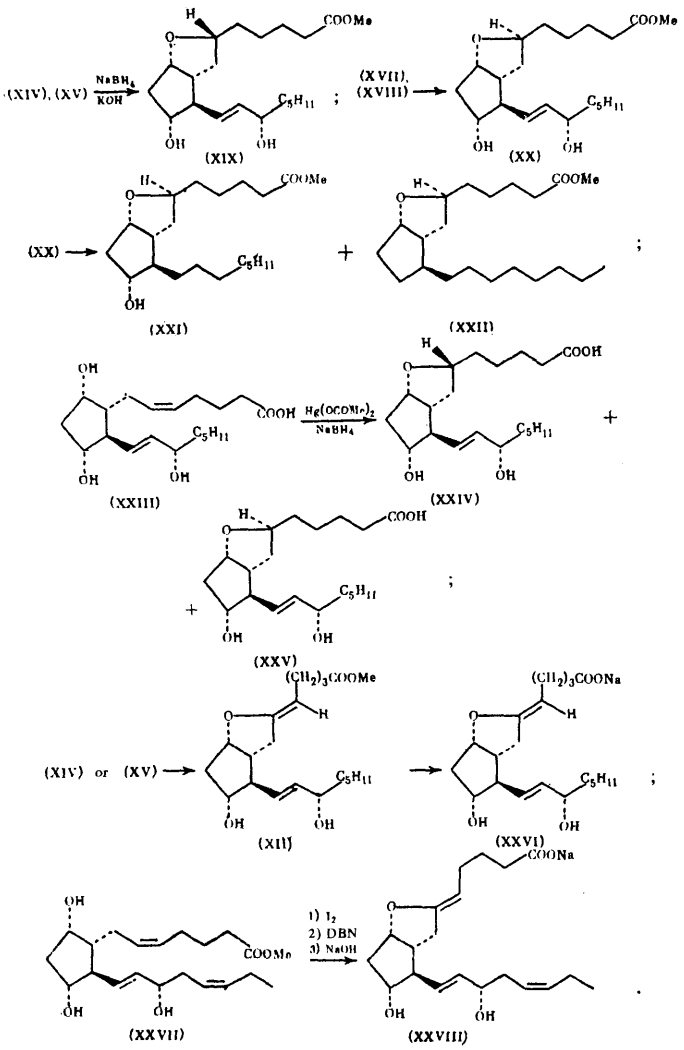
(XII): R = H, R$^1$ = Me

(XIII): R = H, R$^1$ = H

The sodium salts of PC and other compounds with a similar structure, which can be regarded as precursors of PC and its chemically stable analogues, have been synthesised. $PGI_3$ and $\Delta^6$-$PGI_1$ with a double bond in the 6-*endo*-position, have been obtained.[10] The key compounds, the methyl esters of (5*S*, 6*S*)-5-iodo-$PGI_1$ (XIV) and (5*R*, 6*R*)-5-iodo-$PGI_1$ (XV), have been obtained by the reaction of the methyl ester of $PGF_{2\alpha}$ (XIII) with iodine in the presence of sodium carbonate. The diastereoisomeric methyl esters of (5*R*, 6*S*)-5-iodo-$PGI_1$ (XVII) and (5*S*, 6*R*)-5-iodo-$PGI_1$ (XVIII) are formed analogously from the methyl ester of 5-*trans*-$PGF_{2\alpha}$ (XVI). The reductive removal of iodine by treatment with $NaBH_4$ from the esters (XIV) and (XV) or (XVII) and (XVIII) leads to the methyl esters of (6*R*)-$PGI_1$ (XIX) and (6*S*)-$PGI_1$ (XX) respectively. Compounds (XIX) and (XX) can also be obtained by the reaction of compound (XIII) with mercury acetate and subsequent reduction with $NaBH_4$ or from the methyl ester of 6-oxo-$PGF_{2\alpha}$ by treatment with an excess of sodium cyanohydroborate. Catalytic reduction of compound (XX) gives rise to the methyl ester of (6*R*)-13,14-dihydro-$PGI_1$ (XXI) and the methyl ester of (6*S*)-13,14-dihydro-15-deoxy-$PGI_1$ (XXII). The compounds (6*R*)-$PGI_1$ (XXIV) and (6*S*)-$PGI_1$ (XXV), which have structures related to that of $PGI_1$, are obtained by the reaction of $PGF_{2\alpha}$ (XXIII) with mercury acetate and subsequent reduction with $NaBH_4$ or by the hydrolysis of the methyl esters (XIX) and (XX) respectively. The sodium salt of PC (XXVI) can be obtained from the iodo-esters (XIV) and (XV) by reaction with 1,5-diazabicyclo-[4.3.0]non-5-ene (DBN) or with $K_2O$ to form the methyl ester of $PGI_2$ (XII), which gives rise to the sodium salt of $PGI_2$ (XXVI) on treatment with NaOH. Treatment of $PGF_3$ (XXVII) in the same sequence gives rise to the sodium salt of $PGI_3$ (XXVIII) (Scheme 3).

Scheme 3





The racemic 11-deoxy-PC can be obtained analogously from the methyl ester of 11-deoxy-$PGF_{2\alpha}$.[23]

13-Oxa-13,14-dihydro-$PGI_2$ (XXXIII) and 13-thiadihydro-$PGI_2$ have been synthesised from the corresponding $PGF_{2\alpha}$ analogues via the stage involving the formation of the iodoester and subsequent deiodination.[24] The sodium salt (XXXIII) is obtained from the optically active epoxyalcohol (XXIX) whose interaction with the monosodium salt of the diol (XXX) gives rise to 13-oxa-13,14-dihydro-$PGF_{2\alpha}$ (XXXIa). The ester (XXXIb), formed after the esterification of compound (XXXIa), is converted into the iodoester (XXXII). The dehydrohalogenation of compound (XXXII) leads to the methyl ester (XXXIIIa) (90%), whose hydrolysis gives rise to the sodium salt (XXXIIIb).

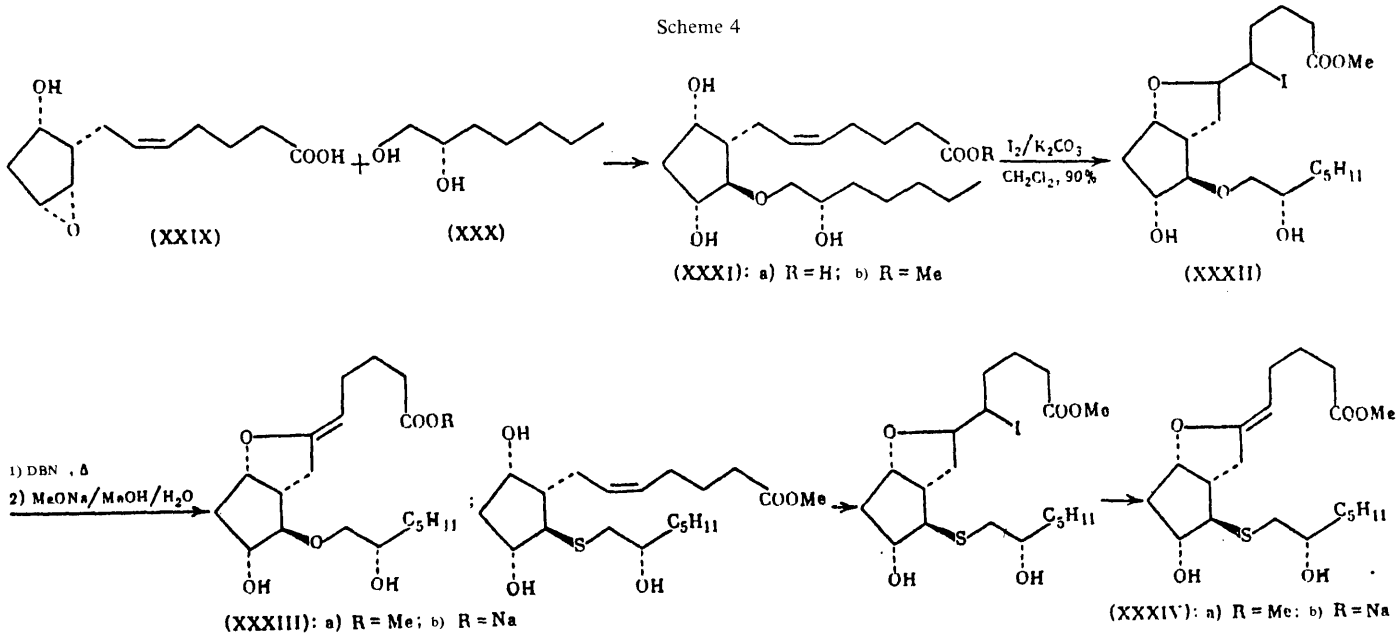
The same procedure was used to obtained the 13-thia-analogue (Scheme 4).

In order to investigate the relation between the reactivity and structure, the sodium salts of native 13-thia-13,14-dihydro-PC and its 15-epi-, 15-methyl-, etc. analogues have been synthesised by a standard method from the corresponding methyl esters of native 13-thia-13,14-dihydro-$PGF_{2\alpha}$ and tested.[25]

A series of sulphur-containing PC have been synthesised stereoselectively by means of the new organoselenium methodology.[26]

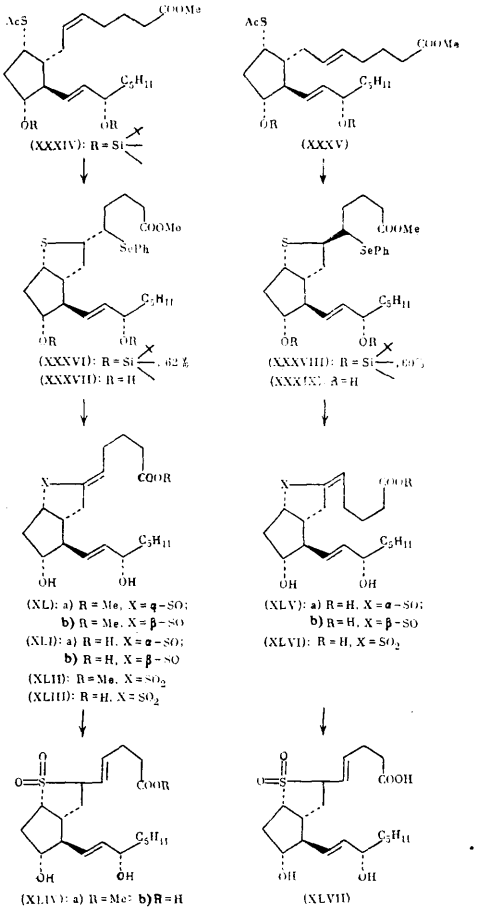
It has been observed that the methyl esters of (5*Z*)- and (5*E*)-$PGF_{2\alpha}$, (XXXIV) or (XXXV), cyclise on treatment with organoselenium compounds without the preliminary removal of the substituent protecting the thiol group. Thus compound (XXXIV) or (XXXV) reacts with phenylselenyl chloride at −78 °C to form the individual selenides (XXXVI) or (XXXVIII), which give rise to compounds (XXXVII) and (XXXIX) after the removal of selenium by treatment with TBAF. It is of interest that, when compound (XXXVII) is treated with the first equivalent of *m*-chloroperbenzoic acid (*m*-CPBA) (at −78 °C), only the sulphur atom is oxidised selectively, while after the addition of the second equivalent of *m*-CPBA at −78 °C and then heating to −20 °C, the selenium atom is oxidised effectively. Further heating to 20 °C leads to the formation of the isomeric (5*Z*)-sulphoxides (XLa) (18%) and (XLb) (53%). On the other hand, when a

Scheme 4



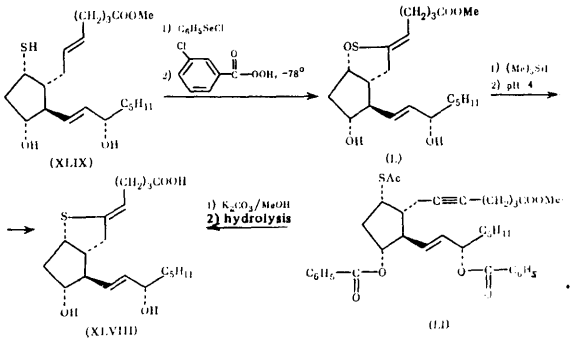
third equivalent of *m*-CPBA is added to the mixture of compounds (XLa, b), the sulphur atom is oxidised further with the exclusive formation of the (5Z)-sulphone (XLII) (86%). This sulphone can be obtained by adding four equivalents of $H_2O_2$ to the reaction mixture of compounds (XLa, b). Finally, the oxidation of the thioselenide (XXXVII) with $H_2O_2$ (8 equivalents, 20 °C) immediately affords the sulphone (XLII) as the main product (75%) together with a small amount of the non-conjugated (4*E*)-sulphone (XLII) (22%). The base hydrolysis of the methyl esters (XLa, b), (XLII), and (XLIVa) leads to the corresponding acids (XLIa, b), (XLIII), and (XLIVb) in satisfactory yields. The acids (XLVa, b), (XLVI), and (XLVII) have been obtained analogously, also in satisfactory yields, from the isomer of the thioselenide (XXXIX) using the oxidation methods described above (Scheme 5).

Scheme 5



The thia-PC (XLVIII) is obtained, like the previous compounds, by the organoselenium method using the methyl ester of 9-thia-5,6-$PGF_{2\alpha}$ (XLIX) as the initial compound. The sulphoxide (L) formed is reduced with iodotrimethylsilane to the corresponding thioether, whose hydrolysis leads to compound (XLVIII).[26-28] The thia-PC (XLVIII) can be obtained in two stages from the prostanoid (LI)[29] (Scheme 6).

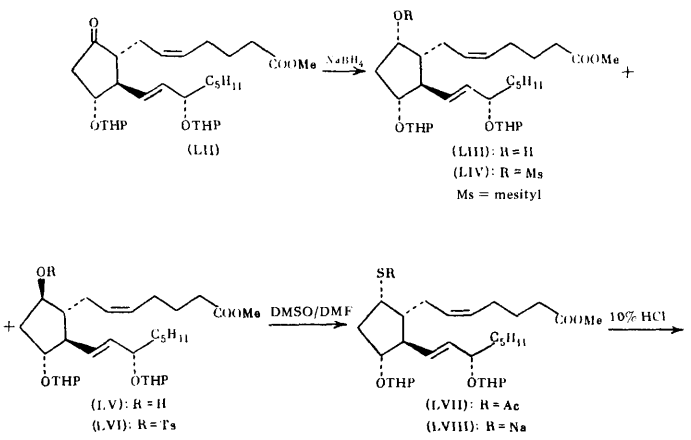
Scheme 6

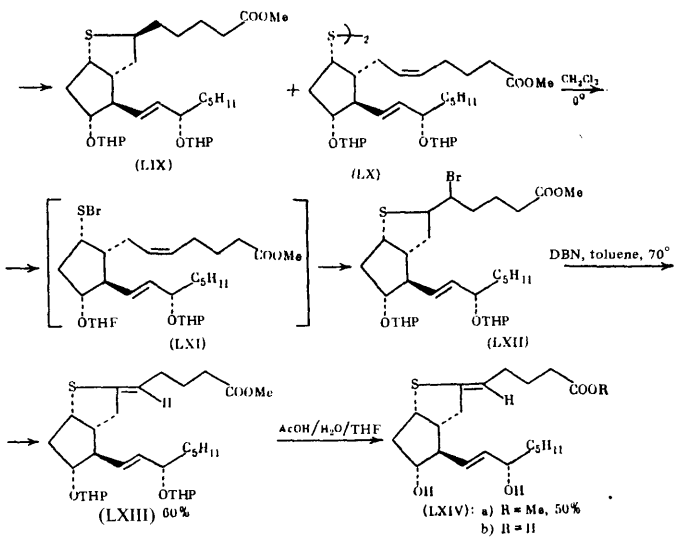


$\Delta^4$-$PGL_1$ has been synthesised from $PGF_{2\alpha}$ by the method described above using organoselenium compounds.[19,20,30,31]

The starting compound in the synthesis of 9(0)-thia-$PGI_2$ is the methyl ester of $PGE_2$ (LII).[32] The reduction of compound (LII) leads to a 1 : 1 mixture of the alcohols (LIII) and (LV). In order to invert the configuration of the 9α-hydroxy-group in compound (LIII), the latter is converted into the methanesulphonate (LIV), the reaction of which with $K_2O$/18-crown-6 ether in DMSO and subsequent esterification with diazomethane afford the 9β-alcohol (LV) (60%). Treatment of the toluene-*p*-sulphonate (LIV) with sodium thioacetate makes it possible to introduce a sulphur atom with simultaneous inversion of the 9β-OH configuration to give the corresponding 9α-derivative (LVII) (55%). Mild hydrolysis of compound (LVII) leads to the cyclic sulphide (LIX) (60%) with a small admixture of the disulphide (LX), formed as a result of oxidation with atmospheric oxygen. The disulphide (LX) is obtained in 80% yield when the mercaptide (LVIII) reaction mixture is kept in atmospheric oxygen. Treatment of compound (LX) with bromine gives rise to the bromosulphide (LVII) and the reaction proceeds via intramolecular cyclisation with the initial formation of the bromosulphide (LXI). Compound (LXII) is then converted into the vinyl sulphide (LXIII) with the required (*syn*, *cis*) geometry). The removal of the protecting group in compound (LXIII) leads to the methyl ester of 9(O)-thia-PC (LXIVa). It is noteworthy that the relatively low yield in the hydrolysis stage indicates the partial decomposition of the final compound (LXIVa). Compound (LXIVa) is converted into compound (LXIVb) by alkaline hydrolysis (Scheme 7).

Scheme 7



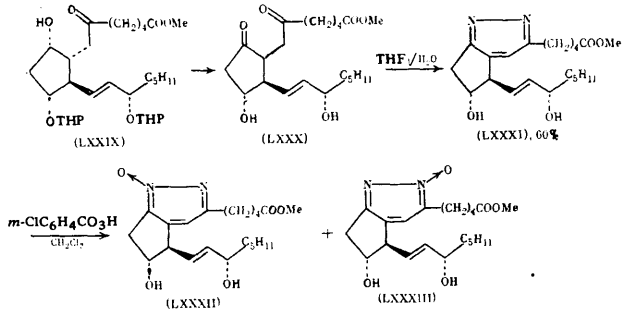


(5Z)- and (5E)-6,9-dithia-PC can be obtained via an analogous scheme from the methyl ester of $PGE_2$.[33]

The synthesis of 9-deoxy-9α,6-nitrilo-$PGF_{1\alpha}$ (LXXII) and of the corresponding cyclic imine in which the oxygen atom has been replaced by nitrogen have been described.[34] The first stage includes the conversion of the methyl ester of $PGF_{2\alpha}$ (LXV) into the 9β-epimer (LXVII) by reaction of compound (LXV) with triphenylphosphine, benzoic acid, and the diethyl ester of azodicarboxylic acid (DEADA) followed by treatment of the resulting 9β-benzoate (LXVI) with MeONa/MeOH. Toluene-*p*-sulphonation of the 9β-hydroxy-group and the removal of the THP protecting groups leads to the derivative monotoluene-*p*-sulphonated at the C(9) atom. Treatment of the 9β-toluene-*p*-sulphonate (LXVIII) with $NaN_3$ affords the 9α-azide (LXIX) which is converted on heating into the cyclic imine (LXXI) (80%). The acid (LXXII) has been obtained by the hydrolysis of the ester (LXXI) or, which is preferable, by the hydrolysis of the ester azide (LXIX) to the acid (LXX) with subsequent cyclisation to the iminoacid (LXXII)—a substance which contains 30% of the zwitter-ionic form. The acid (LXXII) readily gives rise to the hygroscopic hydrochloride (LXXIII), both imines, (LXXI) and (LXXIV), being stable in 1 M HCl solution at 25 °C. The reduction of the iminoester (LXXI) leads to the esters (LXXIVa, b). Both isomers are hydrolysed to the corresponding crystalline iminoacids (LXXVa, b), which exist fully in the zwitter-ionic form. Using the analogous sequence of reactions, the methyl ester of *cis*-$\Delta^4$-$PGF_{1\alpha}$ (LXXVI) was converted in six stages into the 9α,5-nitrilo-analogues (LXXVII) and (LXXVIII) (Scheme 8).

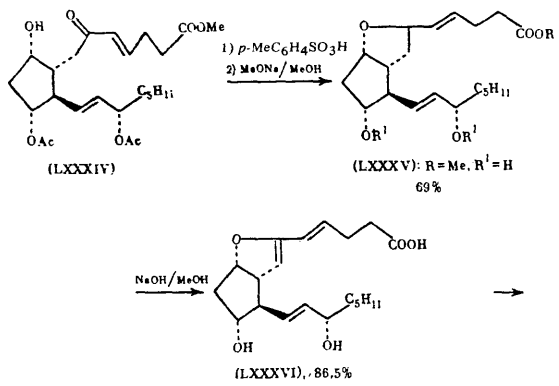
The synthesis of 6,9-pyridazo-PC (LXXXI) and its *N*-oxides (LXXXI), (LXXXII), and (LXXXIII) from the methyl ester of 6-oxo-$PGF_{1\alpha}$ (LXXIX) have been described.[35] Oxidation of compound (LXXIX) with pyridinium chlorochromate of Jones' reagent ($CrO_3$, acetone, −20 °C) and the removal of the THP protecting groups lead to the methyl ester of 6-oxo-$PGE_1$ (LXXX). Treatment of compound (LXXX) with hydrazine and oxidation over $PtO_2$ gives rise to the methyl ester (LXXXI), from which a mixture of the methyl esters (LXXXII) and (LXXXIII) is obtained (Scheme 9).

Scheme 9

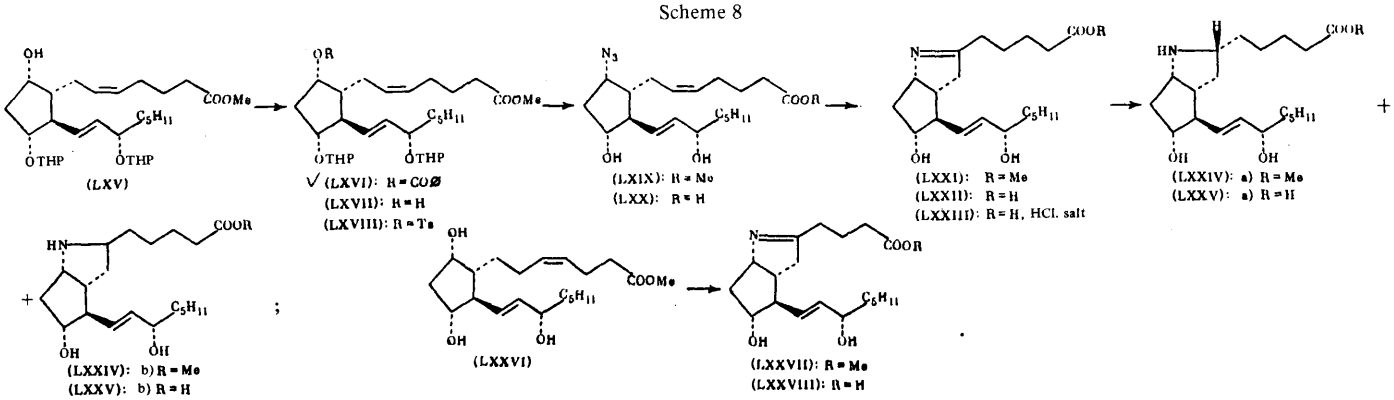


The pyrrole analogue of PC has been obtained from the protected 6-oxo-$PGE_1$ derivative by standard methods.[36]

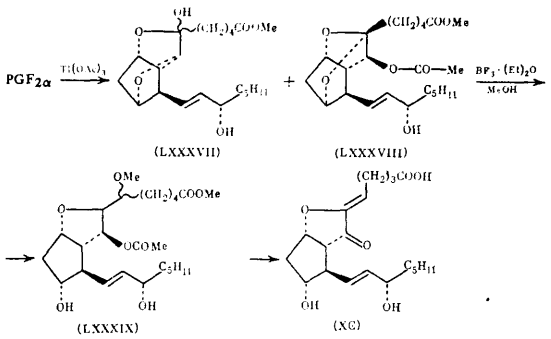
An analogue of $PGI_2$ has been synthesised in two stages from the readily available enone (LXXXIV).[37] After treating the methyl ester of 11(*O*),15(*O*)-diacetyl-4,5-dihydro-6-oxo-$PGF_{1\alpha}$ (LXXXIV) with toluene-*p*-sulphonic acid and subsequent methanolysis, the diene (LXXXV) is obtained whose hydrolysis leads to the isolation of the acid 4,5,6,7-tetrahydro-$PGI_1$ (LXXXVI):



Scheme 8



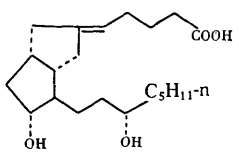
The conversion of the methyl ester of $PGF_{2\alpha}$ into the PC analogue (XC) by the reaction with thallium triacetate, leading to the formation of the hemiacetal (LXXXVII) and the acetate (LXXXVIII), has been described. Transacetylation of compound (LXXXVIII) affords the methyl acetal (LXXXIX), which can be readily converted into 7-oxo-$PGI_2$ (XC) in five stages: [38]



(LXXXVII) (LXXXVIII) (LXXXIX) (XC)

## 2. Synthesis of Carbacyclin

Among the PC analogues, carbacyclin (CC) (XCI) merits special attention. It was reported in 1981 [39] that, when this compound is administered to man intravenously, it causes an appreciable inhibition of platelet aggregation and does not have the side effects observed in the case of PC itself. [16] Carbacyclin can be regarded as a PC derivative in which the ethyl unit in the cyclic enol ether has been replaced by a methylene group:

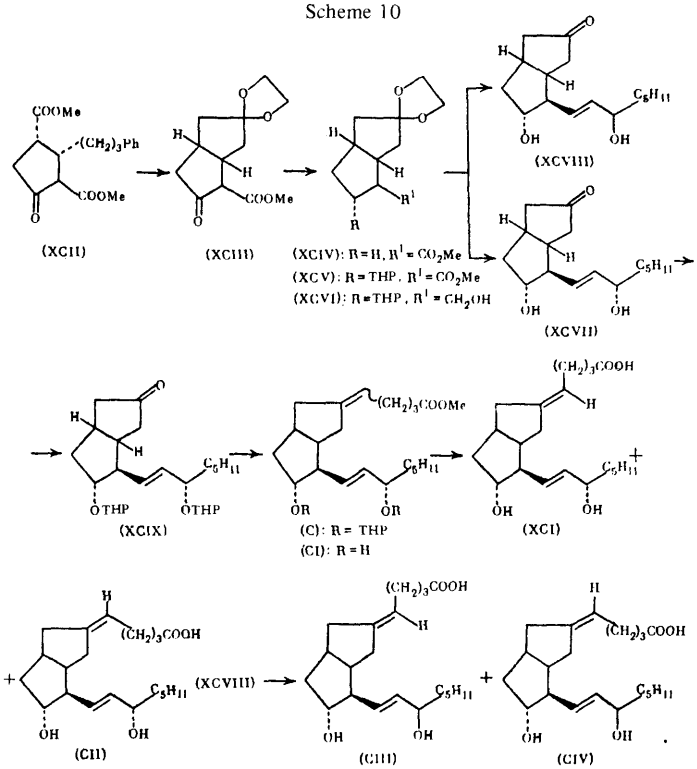


(XCI). CC

Several syntheses of CC were described almost simultaneously, [40–43] representing to some extent a repetition of the classical scheme for the synthesis of PG.

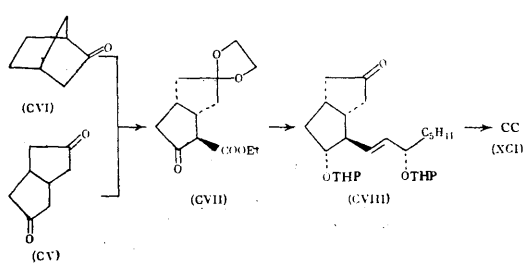
The synthesis of 9(*O*)-methano-PC (XCI) and of its three isomers (CII), (CIII), and (CIV), in which the *trans,cis*-diester (XCII), used in the total synthesis of $PGF_{2\alpha}$, serves as the starting material, has been described. [44] The diester (XCII) is converted in eleven stages into the *cis*-bicyclic ketone (XCIII), whose reduction leads to the basic *trans*-alcohol (XCIV). After protecting the OH group in compound (XCIV) to give a compound (XCV) and after reducing the ester group in the latter with $LiAlH_4$, the alcohol (XCVI) is obtained. The introduction of the allyl alcohol side chain into compound (XCVI) is achieved by standard methods using the diols (XCVII) and (XCVIII): (1) Collins oxidation ($CrO_3$. .$Py/CH_2Cl_2$); (2) condensation with tri-n-butyl-2-oxoheptylidenephosphorane; (3) reduction with $NaBH_4$; (4) the removal of THP protecting groups. After protecting the OH groups in compound (XCVII), the resulting ether (XCIX) is treated with the Wittig reagent obtained from 5-triphenylphosphonopentanoic acid and is then esterified with $CH_2N_2$ to form the ester (C) in the form of a mixture of regioisomers with respect to the C(5) atom. The removal of the protecting groups in compound (C) yields the diol (CI), whose hydrolysis leads to the formation of 9(*O*)-methano-PC (XCI) as the main product and 11α,15α-dihydroxy-6,9α-methyleneprosta-5(*Z*),13(*E*)-dienoic acid (CII); the 5(*E*)-isomer (CIII) and the 5(*Z*)-isomer (CIV) can also be obtained from the diol (XCVIII) by the same sequence of reactions (Scheme 10).

Scheme 10



(XCII) (XCIII) (XCIV): R=H, R¹=CO₂Me (XCV): R=THP, R¹=CO₂Me (XCVI): R=THP, R¹=CH₂OH (XCVII) (XCVIII) (XCIX) (C): R=THP (CI): R=H (XCI) (CII) (CIII) (CIV)

The total synthesis of CC from the readily available *cis*-bicyclo[3.3.0]octane-3,7-dione (CV) in accordance with a similar scheme has been described. [42,44] The most important intermediate in all three syntheses is the monoketal (CVII). In order to prevent the partial hydrolysis of compound (CV) in its conversion to compound (CVII), a method of synthesis of compound (CVII) from 5-norborn-2-enone (CVI) was proposed in 1980. [45] The ester group in compound (CVII) can be converted into an aldehyde whose condensation with the Wittig reagent affords the key ketone (CVIII). It is converted into CC by standard methods:

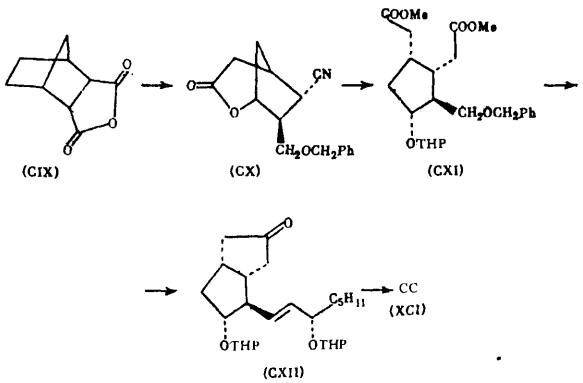


(CVI) (CVII) (CVIII) (CV) CC (XCI)

Three other total syntheses of CC [44,46,47] are based on cyclo-octa-1,3-diene and differ only by the stage in which it is converted into a derivative of *cis*-bicyclo[2.3.0]octan-3-one (CVIII).

A stereocontrolled multistage synthesis of CC from the anhydride of norborn-5-ene-2,3-dicarboxylic acid (CIX) using the methods employed in the synthesis of PG has been proposed. [48] The anhydride (CIX) is converted into the lactone (CX), whose alkaline hydrolysis and the subsequent

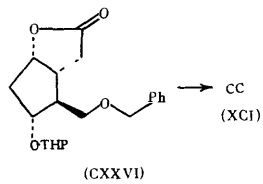
transesterification of the resulting dicarboxylic acid with $CH_2N_2$ lead to the diester (CXI) whose Dieckmann condensation and decarboxylation together with the addition of a side chain at the C(12) atom result in the formation of the CC precursor (CVIII), whose conversion into the CC presents no difficulty. The conversion of compound (CIX) into compound (CVIII) includes 24 stages:




A convenient synthesis of the optically active CC from the hydroxyacid (CXII),[49] which is converted into the cyclic ketone (CXIII), has been described. After protecting the OH group in compound (CXIII), the benzylethyl group in compound (CXIV) is subjected to hydrogenolysis, giving rise to the hydroxyketone (CXV), which is converted into the ester-alcohol (CXVI) (overall yield 77%): protection of the OH group by treatment with 2-methoxypropane, condensation with 4-carboxybutylenetriphenylphosphorane (4-CBTP), selective removal of the 2-methoxypropyl unit, and esterification with $CH_2N_2$. The alcohol (CXVI) is oxidised to the aldehyde (CXVII) using the complex $SO_3$.Py or DMSO-$(COCl)_2$, whose condensation with the phosphonate by the Emmons–Horner method results in the formation of the enone (CXVIII) (99%). After the removal of the THP group in compound (CXVIII), a mixture of the more polar compound (CXIX) and the less polar compound (CXX) is formed (1 : 1, 98%). The selective reduction of the oxo-group at the C(15) atom in compound (CXIX) with diisobutylaluminium 2,6-di-t-butyl-4-methylphenoxide leads to the (15*S*)-alcohol (CXXI) (83%) and the (15*R*)-alcohol (CXXII) (12%). Alkaline hydrolysis of compound (CXXI) gives rise to CC.

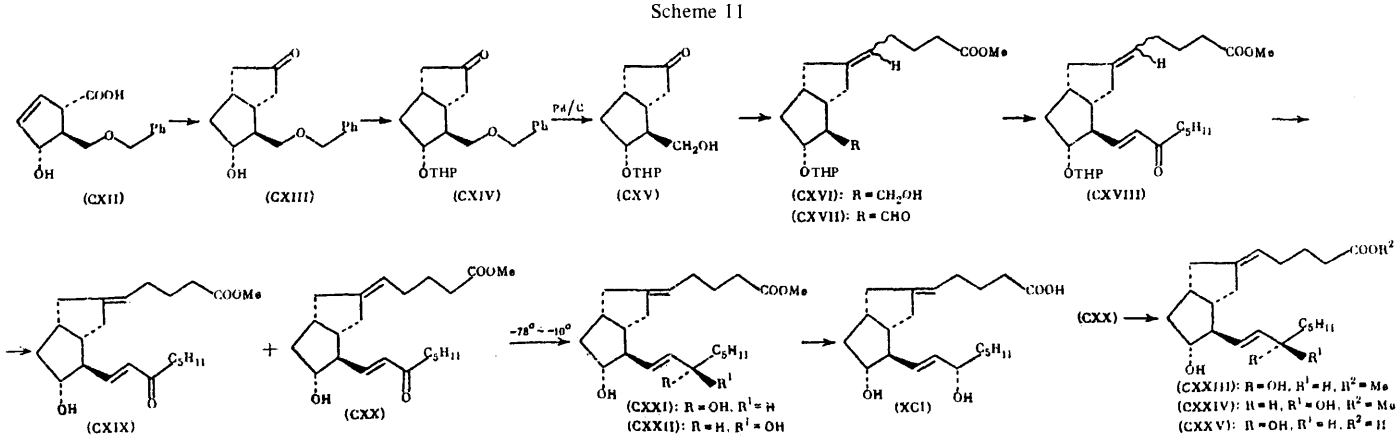
The (5*Z*,15*S*)-isomer (CXXII), the (5*Z*,15*R*)-isomer (CXXIV), and the acid (CXXV) are obtained from the enone (CXX) in the same way (Scheme 11).

CC can also be obtained from the lactone (CXXVI), which is used in the synthesis of natural PG:[49]

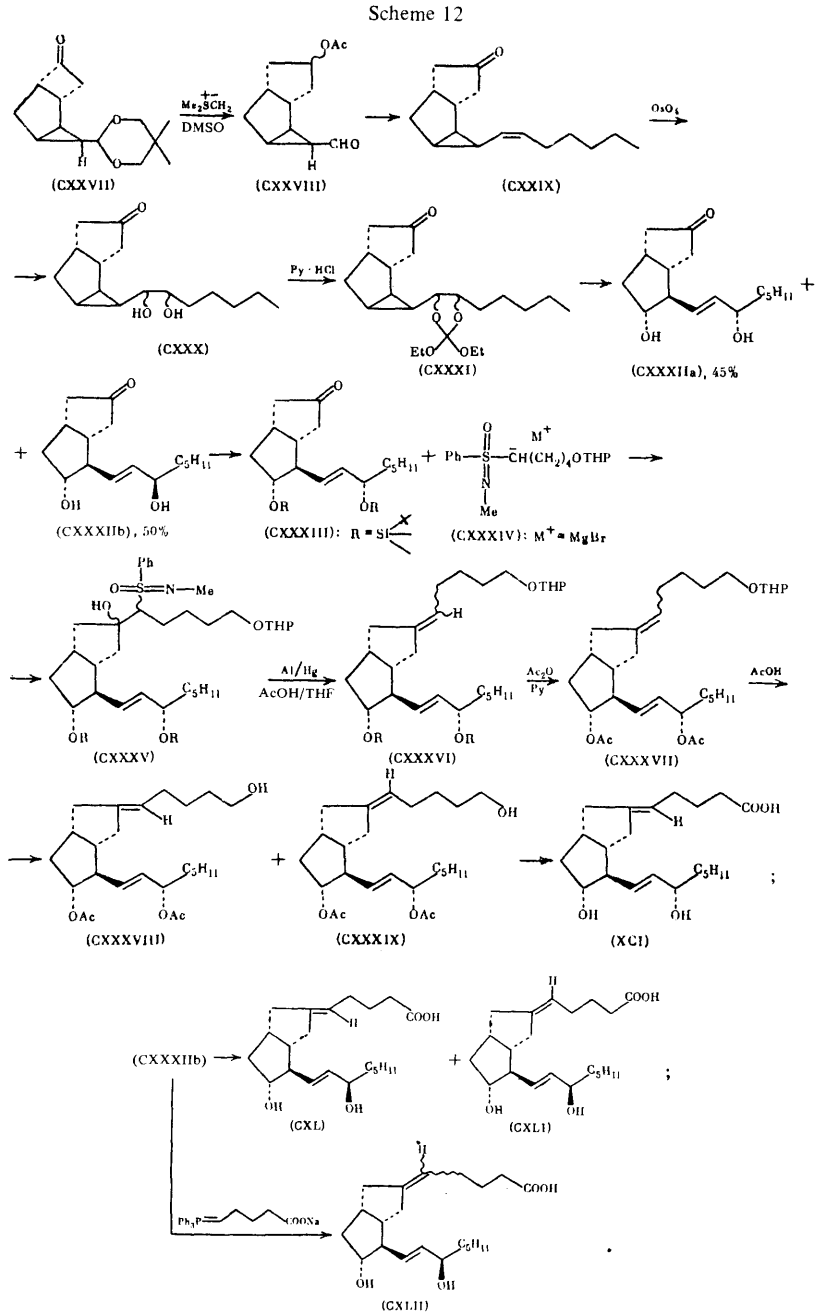



One of the ways of synthesising optically active CC involves the use of the familiar intermediate optically pure ketone (CXXVII),[40] which is converted into the *endo*-aldehyde (CXXVIII) when the latter is successively condensed with n-hexylidenetriphenylphosphorane, hydrolysed, and oxidised by Jones' reagent with formation of the tricyclic intermediate (CXXIX). The ketone (CXXIX) is converted into the isomeric *cis*-glycols (CXXX). The reaction of compound (CXXX) with triethyl orthopropionate affords the isomeric orthoesters (CXXXI), which are converted into the (15*S*)-ketonediol (CXXXIIa) and the (15*R*)-ketonediol (CXXXIIb) after solvolysis in 100% formic acid and alkaline hydrolysis. The condensation of the ketone (CXXXIII) with the anion of the sulphoxyimine (CXXXIV) leads to a mixture of adducts (CXXXV), which give rise to the isomeric [with respect to the C(5) atom] olefins (CXXXVI) on reductive elimination. The silyl groups are removed with TBAF and the diols formed are converted into the isomeric diacetates (CXXXVII). After removing the protecting group at the C(1) atom in compound (CXXXVII), a mixture of the unsaturated alcohols (CXXXVIII) is oxidised by Jones' reagent and hydrolysed with aqueous alkali to CC. Using the same methods, the corresponding (15*R*)-dihydroxy acids (CXL) and (CXLI) were obtained from the (15*R*)-ketonediol (CXXXIIb). Condensation of the ketonediol (CXXXIIb) with the Wittig reagent gives rise to a mixture of the C(5)-isomers and the dihydroxyacids (CXII) (Scheme 12).

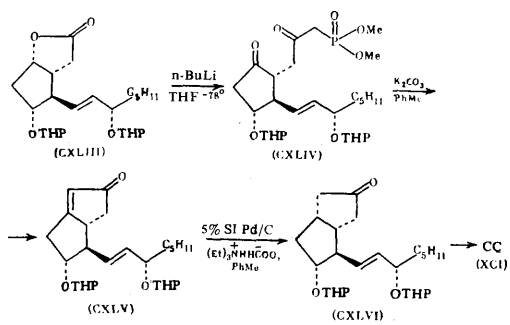
Scheme 11



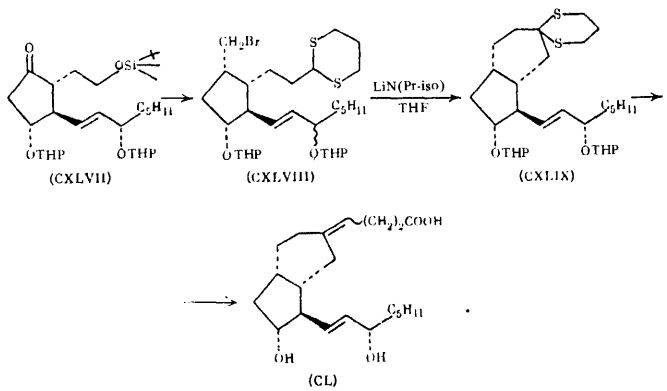
Scheme 12



The synthesis of CC via the key intermediate (CXLIII) has been described.[50,51] The reaction of compound (CXLIII) with the lithio-derivative of dimethyl methylphosphonate leads to a bicyclic alcohol, whose Collins oxidation produces the ketone (CXLIV). A suspension of the latter in 18-crown-6 ether is heated, the enone (CXLV) is obtained and its reduction affords compound (CXLVI). The condensation of the latter with 4-CBTP and subsequent removal of the THP protecting group leads to CC:

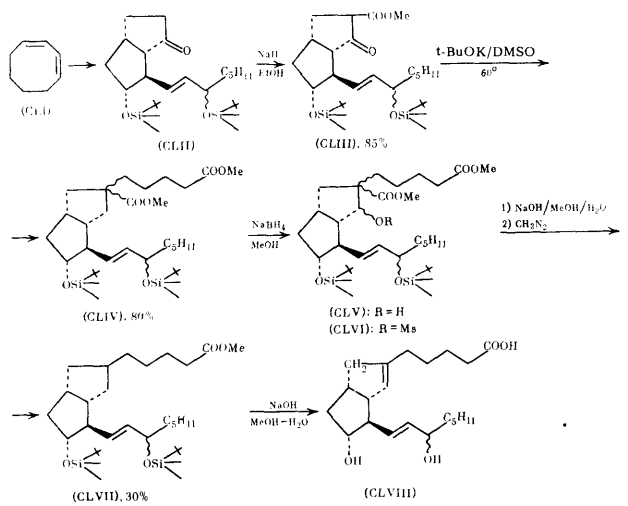


The 11-stage synthesis of 6a-carba-$PGI_2$ (CL) from the ketone (CXLVII) has been achieved.[52] The intermolecular alkylation of the dithiane (CXLVIII), obtained from compound (CXLVII) by the usual methods in 7 stages, is the key stage in the formation of the bicyclic compound (CXLIX), which is converted into compound (CL) in three stages:



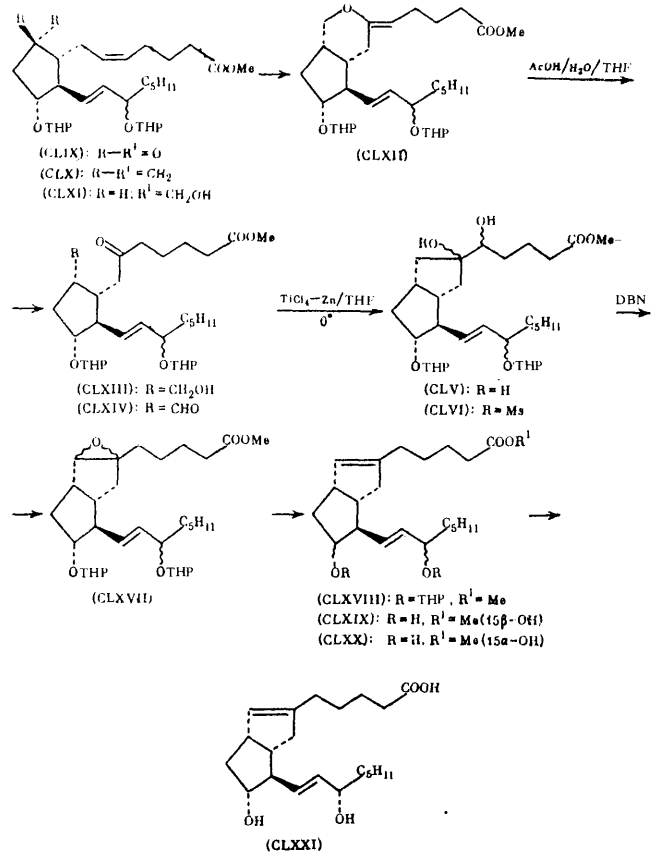

A method of synthesis of the carbon analogue $\Delta^6$-PGI (CLVIII), using cyclo-octa-1,3-diene (CLI) as the starting compound, has been described.[53] The regioselective methoxycarbonylation of the ketone (CLII), obtained in 7 stages from compound (CLI), with dimethyl carbonate leads to the ketoester (CLIII). The reaction of compound (CLIII) with methyl 5-iodoheptanoate yields the alkylated product (CLIV) in the form of a mixture of stereoisomers with respect to the C(6) atom. The reduction of the ketone (CLIV) leads to a mixture of the diastereoisomeric alcohols (CLV) (90%), the methanesulphonation of which affords compound (CLVI). The decarboxylation and subsequent esterification of compound (CLVI) lead to the ester (CLIII). Despite the low yields of compound (CLIII), this synthesis has the advantage that the methoxycarbonyl functional group at the C(6) atom not only makes it possible to carry out successfully the alkylation at the C(6) atom but also promotes the introduction of a double bond between the C(5) and C(6) atoms. After the removal of the protecting groups in compound (CLVII) and hydrolysis, 9(*O*)-methano-$\Delta^6$-$PGI_1$ (CLVIII) is isolated in the form of a mixture of diastereoisomers with respect to the C(15) atom (the 15α- and 15β-isomers) (Scheme 13).

Scheme 13




Using an intermolecular pinacol addition reaction as the key stage, 9(*O*)-methane-$\Delta^{6(9\alpha)}$-$PGI_1$ (CLXXI) was obtained.[54-57] The methylene group in the $PGE_2$ (CLIX) molecule is introduced by treatment with $Zn-CH_2Br_2-TiCl_4$, which results in the formation of compound (CLX) (80%). Cautious hydroboration of compound (CLX) with 9-borabicyclo[3.3.1]nonane (9-BBN) (THF, 0°) followed by treatment with an $H_2O_2$ solution leads to the primary alcohol (CLXI) (64.5%). The iodoesterification of the latter and treatment with DBN yield the enol ether (CLXII) (the main product), which is converted into the ketoalcohol (CLXIII). The oxidation of compound (CLXIII) with the complex $SO_3$.Py leads to the aldehyde (CLXIV), which is immediately introduced into the intermolecular pinacol addition reaction with formation of a mixture of the diastereoisomeric bicyclic diols (CLXV). The crude compound (CLXV) is converted into the methanesulphonate (CLXVI), which is in turn converted into the epoxy-derivative (CLXVII) and then into the *endo*-olefin (CLXVIII). After the removal of the THP protecting groups, a readily separable mixture of alcohols is obtained [the less polar 15β-isomer (CLXIX) and the more polar 15α-isomer (CLXX)]. Alkaline hydrolysis of compound (CLXX) leads to compound (CLXXI) (Scheme 14).

Scheme 14

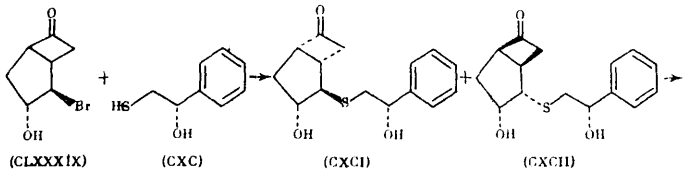



Using the intramolecular thermal ene reaction, (+)-9(*O*)-methano-$\Delta^{6(9\alpha)}$-$PGI_1$ (CLXXXVIII) was synthesised from the Corey lactone.[58] The aldehyde (CLXXVIII), necessary for the ene reaction, is obtained by converting the lactone (CLXXII) into the hydroxyester (CLXXIII) in the usual way: (1) reduction with diisobutylaluminium hydride (DIBAH); (2) condensation with 4-CBTP; 3) esterification with $CH_2N_2$ (overall yield 98%). The subsequent oxidation of compound

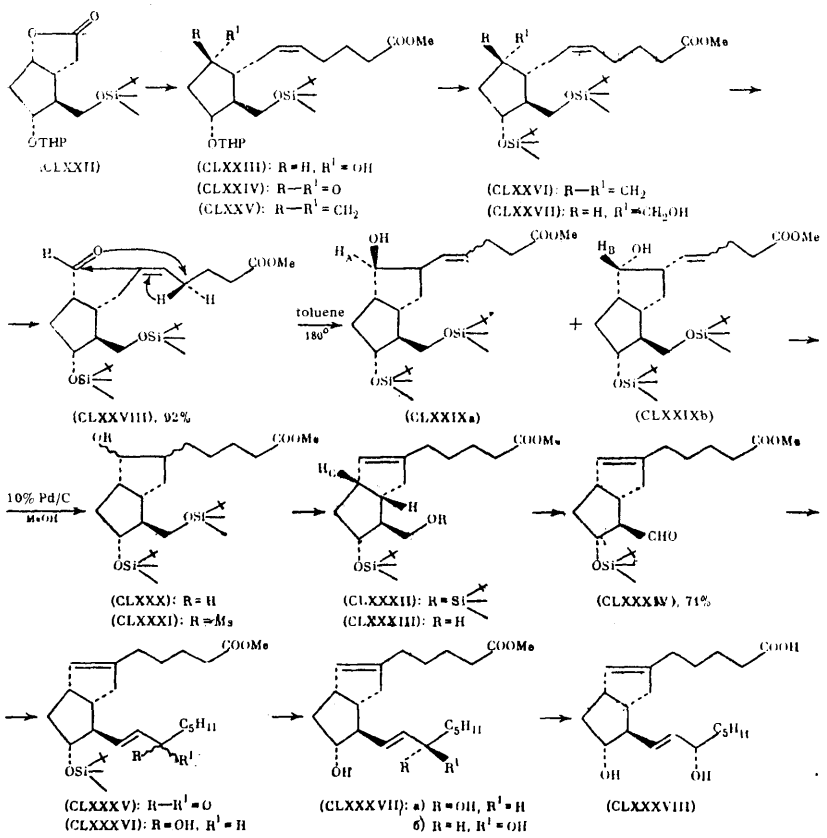
(CLXXIII) with pyridinium chlorochromate gives rise to the ketoester (CLXXIV) (92%). Substitution of the methylene group in the latter by treatment with $Zn-CH_2Br_2-TiCl_4$ leads to the diene (CLXXV) (81%). The thermally unstable THP-ether (CLXXV) is converted in two stages into the disilyl ether (CLXXVI), the hydroboration of which with 9-BBN and subsequent treatment with a solution of $H_2O_2$ produces the primary alcohol (CLXXVII), which is converted by the Collins oxidation into the aldehydes (CLXXVIII). The thermal ene reaction at 180 °C leads to two ene products: (CLXXIXa) (the main more polar isomer) and (CLXXIXb) (the minor less polar isomer). The mixture of these compounds is hydrogenated, which affords compound (CLXXX). On heating with diazabicycloundecene (DBU), the methanesulphonate (CLXXXI) gives rise to compound (CLXXXII). On treatment of the latter with a catalytic amount of pyridinium toluene-*p*-sulphonate, one obtains the key intermediate (CLXXXIII), whose oxidation produces the aldehyde (CLXXXIV), which condenses, without being isolated, with dimethyl 2-oxoheptylphosphonate to form the enone (CLXXXV) (71%). The reduction of compound (CLXXXV) with $NaBH_4$ gives rise to the C(15)-epimeric alcohols (CLXXXVI) and the removal of the protecting group leads to the more polar diol (CLXXXVIIa) (55%) and the less polar diol (CLXXXVIIb) (22%). Alkaline hydrolysis of compound (CLXXXVIIa) results in the formation of compound (CLXXXVIII) (Scheme 15).

An 8-stage synthesis of a CC analogue, namely the benzamidophenyl ester of (CC), has been achieved in 5% yield.[59] The key compounds for the synthesis of this analogue are the bromohydrin (CLXXXIX) and the thiol (CXC), which are in their turn obtained from cyclopentadiene and L-(+)-mandelic acid respectively. The addition of compound (CXC) to the bromohydrin (CLXXXIX) leads to a mixture of the isomers (CXCI) and (CXCII) which is difficult to separate. Treatment of the mixture with $CH_2N_2$ makes it possible to carry out a ring expansion reaction. The resulting mixture of compounds (CXCIII), (CXCIV), (CXCV), and (CXCVI) is readily separated by chromatography on silica gel. The Wittig condensation of compound (CXCIII) with the phosphorane obtained from phosphonium salts (CXCVII) results in the formation of a mixture of the *E*- and *Z*-isomers (CXCVIII) and (CXCIX), which is esterified with *p*-benzamidophenol and compound (CC) is isolated (Scheme 16).

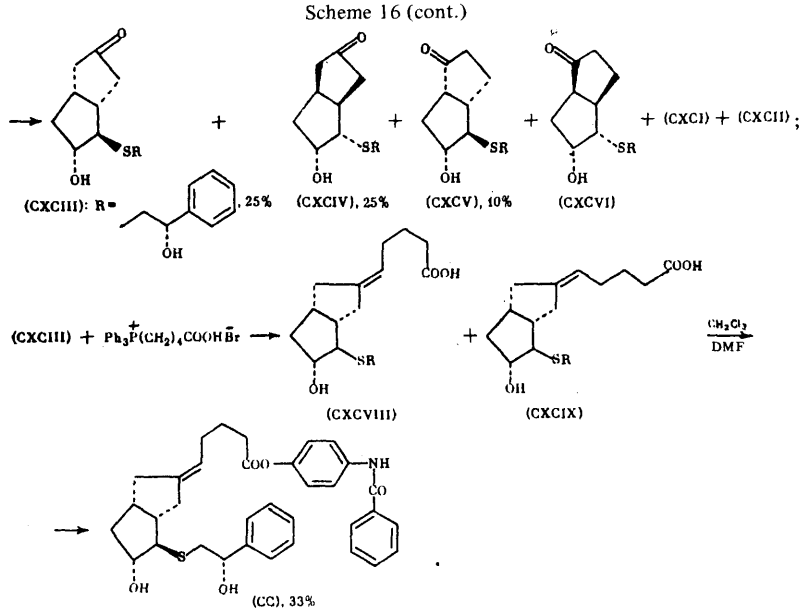
Scheme 16




Scheme 15

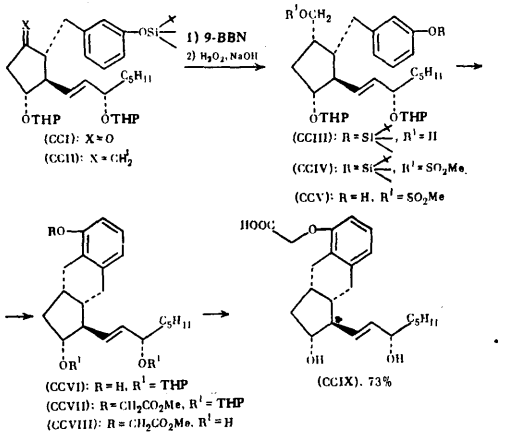


Scheme 16 (cont.)



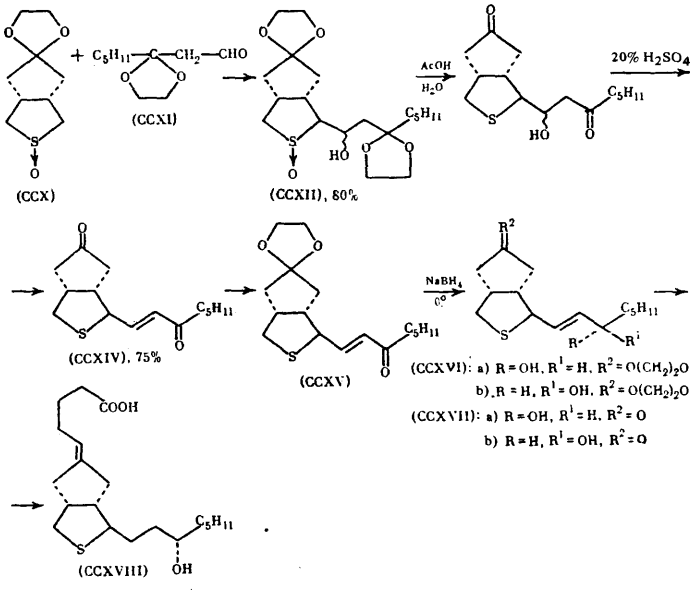

In order to discover PC analogues which are resistant to hydrolysis, benzoindene derivatives have been synthesised.[60,61] The starting material for the synthesis of such derivatives was compound (CCI), which is used in the synthesis of PG analogues.[62] The methylene group is introduced in two stages: the ketone reacts with the anion of methylphenyl-*N*-methylsulphoxyimine and this is followed by treatment of the adduct with aluminium amalgam ($H_2O$–AcOH–THF) with formation of compound (CCII) (72%), whose hydroboration and subsequent oxidation produce the alcohol (CCIII) (92%). The alcohol (CCIII) is converted into the methanesulphonate (CCIV) (88%), the silyl group in the latter is removed by treatment with TBAF, and compound (CCV) is refluxed with NaH in glyme until the formation of compound (CCVI), which is converted into the ester (CCVII) by treatment with NaH and methyl bromoacetate. After the removal of the THP protecting group, the ester (CCVIII) is formed and its alkaline hydrolysis affords the crystalline acid (CCIX) (Scheme 17).

Scheme 17

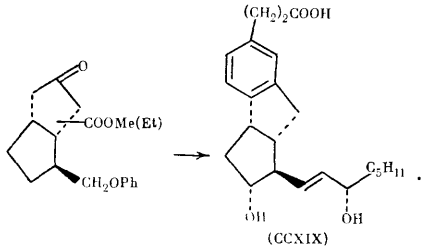



The synthesis of the ethylene ketal of tetrahydrobiscyclopentano[c]thiophen-5-one (CCX) and its conversion into the analogue 11-thia-CC have been described.[63] The synthone (CCX) has two functional groups, which makes it possible to introduce the necessary side chain fairly readily and also has a hydrogen atom activated by the sulphoxide group. The introduction of the ω-chain into the molecule is achieved by the reaction of the carbanion generated from compound (CCX) with the protected aldehyde (CCXI) to form a mixture of the aldols (CCXII), which is not separated. Treatment of the mixture with diborane with subsequent deketalisation leads to the formation of the β-hydroxyketone (CCXIII), whose dehydration affords the αβ-*trans*-enone (CCXIV). The ring carbonyl group is protected by treatment with 2-ethyl-2-methyl-1,3-dioxolan and compound (CCXV) formed is reduced to a mixture of the epimeric alcohols (CCXVIa, b). After the removal of the ketal protecting group, the mixture of compounds (CCXVIIa, b) is separated chromatographically. The condensation of the more polar C(15)-epimer (CCXVIIa) with 4-CBTP leads to compound (CCXVIII) and its (15*R*)-epimer in the form of a mixture of the *cis*,*trans*-isomers (Scheme 18).

Scheme 18



In order to establish the relation between structure and activity for a series of $PGI_2$ analogues, a new aromatic CC analogue (CCXIX), which has no biological PC activity, was obtained by total synthesis (20 stages):[64]




(CCXIX)

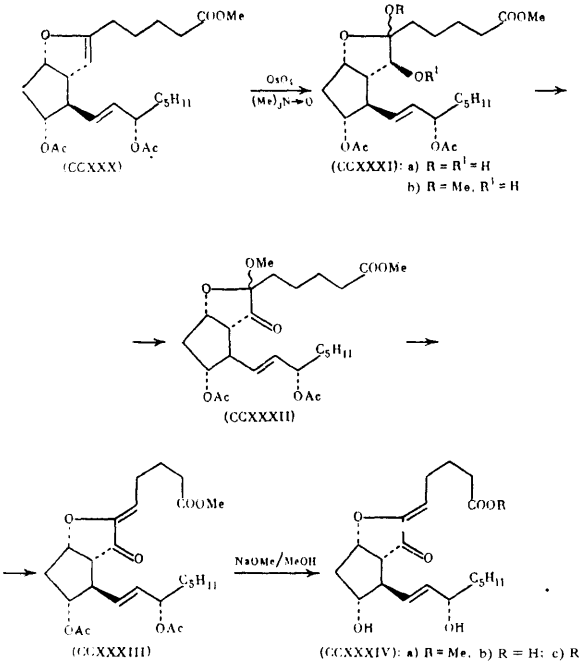
### 3. The Synthesis of Prostacyclin Analogues with an Enol Ether Double Bond Resistant to Hydrolysis

One of the effective ways of stabilising PC involves the introduction of electron-donating and electron-accepting substituents next to the enol ether group sensitive to hydrolysis or its replacement by another ether system.

Thus halogenation of the protected ethyl ester of $PGI_2$ (CCXX) proceeds stereoselectively with formation of the methyl ester of (5*R*)-5-Cl-$\Delta^6$-$PGI_1$ (CCXXIIa) (60%) or the methyl ester of (5*R*)-5-Br-$\Delta^6$-$PGI_1$ (CCXXIIb) (57%) with an admixture of the succinimido-adduct (CCXXIVa) (20%) or compound (CCXXIVb) (20%).[65] On the other hand, the halogenation of the acetyl-substituted methyl ester of $PGI_2$ (CCXXI) under the same conditions gives rise to a mixture of the diastereoisomers of the methyl ester of 5-Cl-$\Delta^6$-$PGI_2$ (CCXIIIa) (58%, 5*R* : 5*S* = 5 : 3) or the methyl ester of 5-Br-$\Delta^6$-$PGI_1$ (CCXXIIIb) (60%, 5*R* : 5*S* = 7 : 3) with the corresponding succinimido-adduct (CCXXIVc) (20%) or (CCXXIVd) (13%). The subsequent chlorination of the (5*R*)-allyl chloride (CCXXIIa) with *N*-chlorosuccinimide NCS leads to a mixture of the methyl esters of (5*E*,7*S*)- and (5*Z*,7*S*)-5,7-dichloro-$PGI_2$ (CCXXV) and (CCXXVI) (15 and 20% respectively). Treatment of the allyl chloride (CCXXIIa) with Py.TsOH leads to the hemiacetal (CCXXVII), whose dehydration with an excess of $MgSO_4$ in benzene results in the formation of the (5*E*)-vinyl chloride (CCXXVIIIa) (20%) and the (5*Z*)-vinyl chloride (CCXXIXa) (28%). The removal of the protecting groups in compounds (CCXXVIIIa) and (CCXXIXa) with TBAF leads to the methyl esters of (5*E*)-5-Cl-$PGI_2$ (CCXXVIIIb) (95%) and (5*Z*)-5-Cl-$PGI_2$ (CCXXIXb) (80%), whose alkaline hydrolysis resulted in the formation of the sodium salts (CCXXVIIIc) and (CCXXIXc) (Scheme 19).

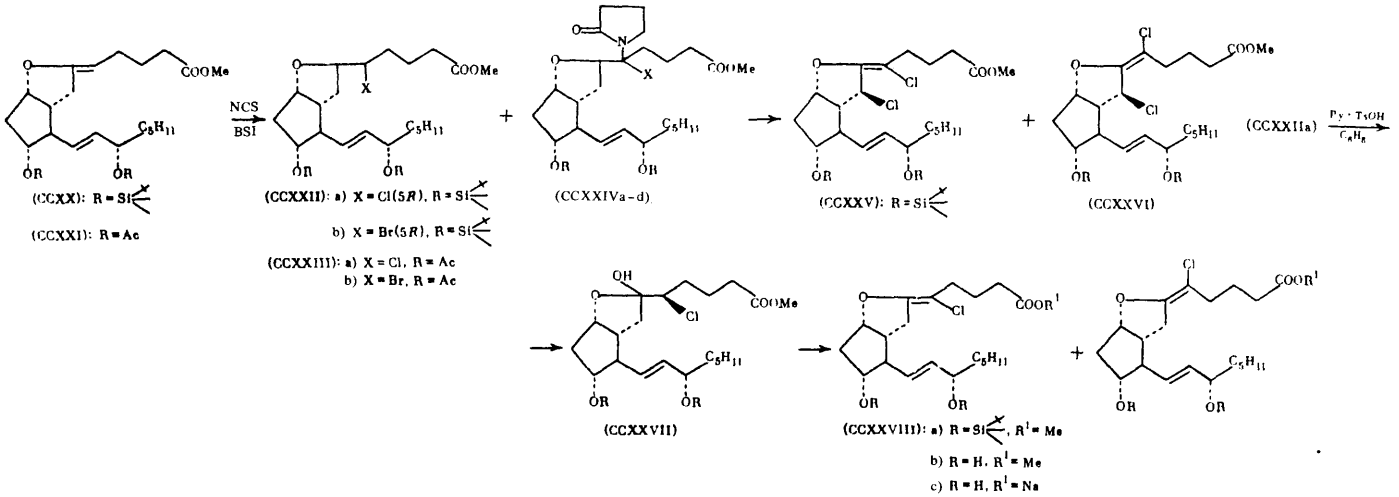
A five-stage synthesis of 7-oxo-$PGI_2$ (CCXXXIV) via the selective hydroxylation of the methyl ester of 11,15-diacetyl-$\Delta^6$-$PGI_1$ (CCXXX) has been described. The stereochemistry of the intermediates has been determined and their conformational analysis has been carried out.[66] Selective hydroxylation of the enol ether double bond in compound (CCXXX) proceeds smoothly with formation of compound (CCXXXIa) (80%), which is converted into the isomeric methyl ketals by appropriate successive treatments (MeOH, $Et_2O.BF_3$); after chromatographic separation one obtains the pure *endo*-isomer (27%) and exo-isomer (51%) of compound (CCXXXIb). Oxidation of both isomers (pyridinium dichromate/DMF or pyridinium chlorochromate/NaOAc/$CH_2Cl_2$) leads to the *endo*- and *exo*-isomers of compound (CCXXXII) respectively, whose thermolysis at 160–170 °C affords compound (CCXXXIII) and deacetylation of the latter results in the formation of compound (CCXXXIV) (Scheme 20).

Scheme 20



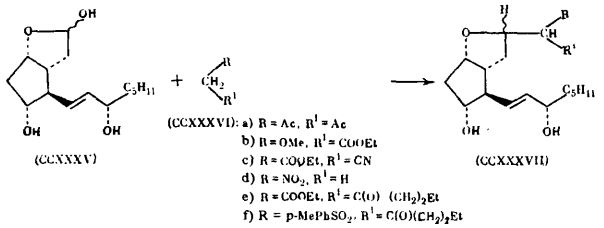

(CCXXX) (CCXXXI): a) R = R¹ = H; b) R = Me, R¹ = H (CCXXXII) (CCXXXIII) (CCXXXIV): a) R = Me, b) R = H; c) R = Na

Scheme 19

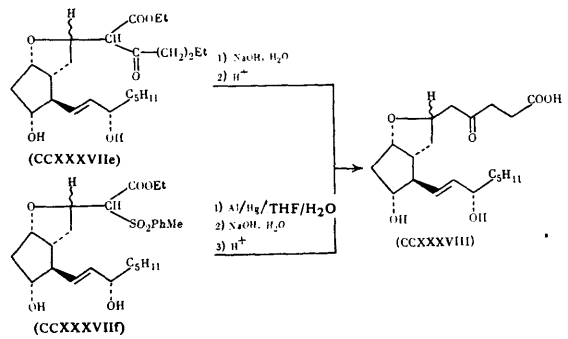



(CCXX): R = Si (CCXXI): R = Ac (CCXXII): a) X = Cl(5*R*), R = Si; b) X = Br(5*R*), R = Si (CCXXIII): a) X = Cl, R = Ac; b) X = Br, R = Ac (CCXXIVa–d) (CCXXV): R = Si (CCXXVI) (CCXXVII) (CCXXVIII): a) R = Si, R¹ = Me; b) R = H, R¹ = Me; c) R = H, R¹ = Na

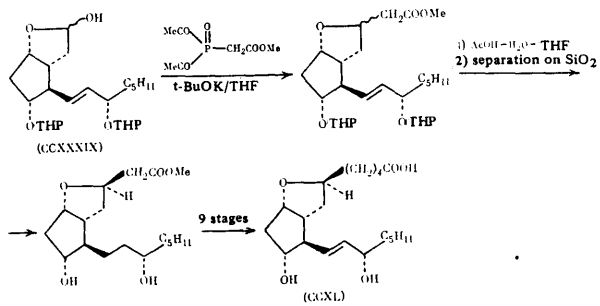
A simple method of synthesising the PC analogues (CCXXXVII) using the hemiacetal (CCXXXV) and a compound with an active methylene group [compounds (CCXXXVIa–f)] under the conditions of the Knoevenagel condensation has been proposed:[67,68]



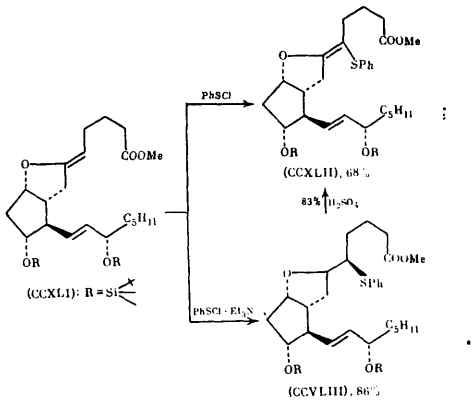

This method is extremely promising, since many compounds with an active methylene group can be condensed. The reaction can be carried out both with malonic and acetoacetic acid derivatives and with β-oxosulphones and aliphatic nitro-compounds. An advantage of this method is its simplicity, which makes it possible to apply it on an industrial scale. Despite the fact that the reaction results in the formation of all four possible isomers of compound (CCXXXVII), the Knoevenagel condensation has been used successfully as the key stage in the synthesis of the familiar 4-oxo-$PGI_1$ (CCXXXVIII):




An analogous strategy has been used to convert the lactone (CCXXXIX) into 6β-$PGI_1$ (CCXI), the Wittig condensation being used in the first stage instead of the Knoevenagel condensation:[69]

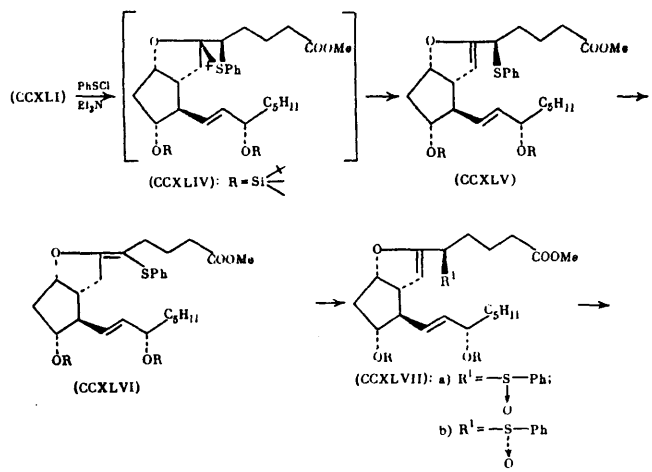


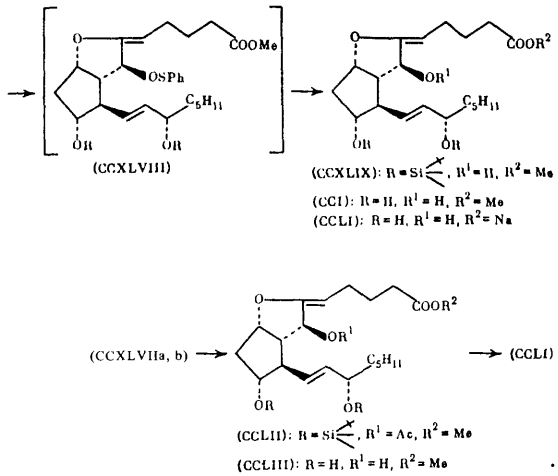

Several stable $PGI_2$ analogues containing electron-accepting substituents at the C(5) or C(7) atoms have been synthesised.[70] The methyl ester of $PGI_2$ (CCXLI) reacts with benzenesulphenyl chloride to form (5*E*)-5-phenylthio-$PGI_2$ (CCXLII) or (5*R*)-5-phenylthio-$\Delta^6$-$PGI_1$ (CCXLIII) depending on the condensation conditions.




The synthesis of the stable analogues 7-hydroxy- and 7-acetoxy-$PGI_2$, the methyl ester of $PGI_2$, using the stereocontrolled sulphoxide–sulphenate rearrangement has been described.[71] The methyl ester (CCXLI) is converted into the allyl sulphide (CCXLV) (86%), the phenylthio-group attacking the less hindered β-side of the $\Delta^5$-double bond with formation of the intermediate episulphonium ion (CCXLIV), in which the proton at the C(7) atom is abstracted with conversion into compound (CCXLV). It is of interest that, when a solution of compound (CCXLV) in $CHCl_3$ is treated with a catalytic amount of $H_2SO_4$, the $\Delta^6$-double bond isomerises rapidly and readily to the (5*E*)-sulphide (CCXLVI) (83%) without the formation of the (5*Z*)-isomer. The oxidation of compound (CCXLVI) with *m*-chloroperbenzoic acid gives rise to an isomeric mixture of the sulphoxides (CCXLVIIa, b) (53%), which is not resolved into the isomers in view of the rapid epimerisation of allyl sulphoxides via the sulphenate ester (CCXLVIII) stage [(CCXLVIIa) ⇌ (CCXLVIII) ⇌ (CCXLVIIb)]. When a mixture of compounds (CCXLVIIa, b) is treated with diethylamine, the rearranged alcohol (CCXLIX) is obtained (68%). The silyl protecting groups in the latter are removed with TBAF to form the methyl ester of (7*S*)-hydroxy-$PGI_2$ (CCL) (87%), the alkaline hydrolysis of which affords the sodium salt of (7*S*)-hydroxy-$PGI_2$ (CCLI). Treatment of compounds (CCXLVIIa, b) with the acetic acid–pyridine mixture yields the acetate (CCLII) (62%). The removal of the protecting groups with TBAF leads to the methyl ester of (7*S*)-acetoxy-$PGI_2$ (CCLIII), whose hydrolysis results in the formation of compound (CCLI) (Scheme 21).

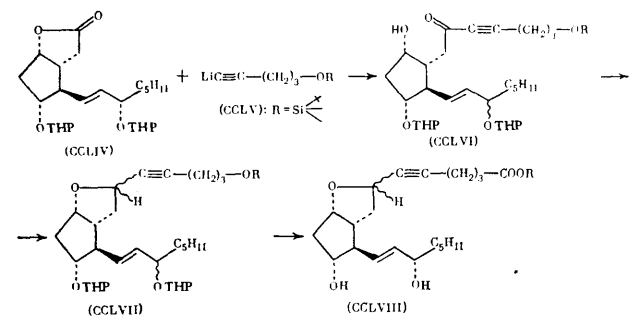
Scheme 21





An interesting synthesis, involving only a few stages, of the 4,4,5,5-tetrahydro-PC analogue (CCLVIII) has been developed.[72] The initial compound employed was the lactone (CCLIV), whose reaction with alkynyl-lithium (CCLV) results in its conversion into the ketone (CCLVI). The reduction of the keto-group with $NaBH_4$ and subsequent cyclisation in the presence of toluene-*p*-sulphonyl chloride in pyridine lead to the bicyclic compound (CCLVII). After the removal of the THP group in the usual way and alkaline hydrolysis, the latter is converted into compound (CCLVIII) (Scheme 22).

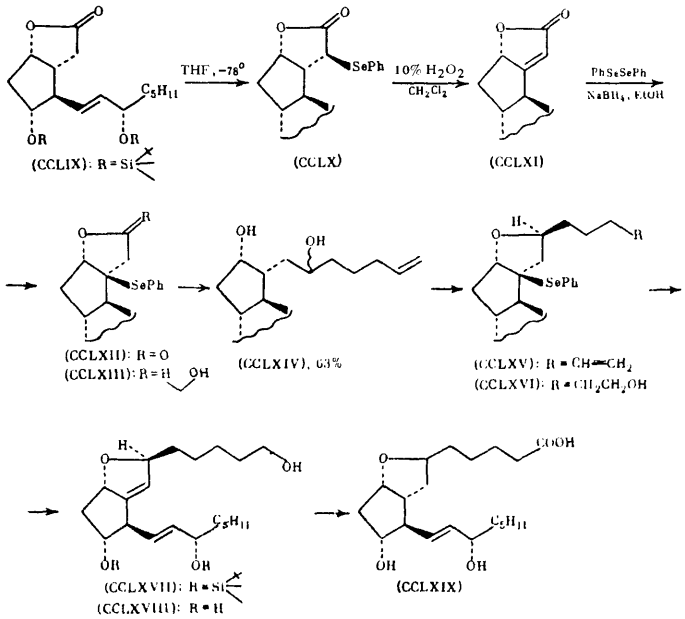
Scheme 22



A similar strategy, based on the use of the lactone (CCLIV), was used in the synthesis of 6β-$\Delta^7$-$PGI_1$.[73]

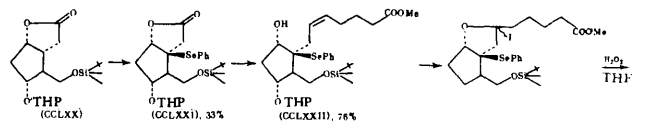
The synthesis of (6*R*)- and (6*S*)-$\Delta^7$-$PGI_1$ (CCLXIX) [74] from the lactone (CCLIX) has been described. The reaction of the lactone with lithium diisopropylamide and treatment of the resulting enolate with PhSeCl yield the 7-phenylselenyl-lactone (CCLX) (90%), which is converted into the αβ-unsaturated lactone (CCLXI) via the phenylselenium oxide elimination stage. The lactone (CCLXI) is converted into the 8-phenylselenolactone (CCLXII), whose reduction with DIBAH gives rise to the lactone (CCLXIII). The alkylation of compound (CCLXIII) with 4-pentylmagnesium bromide leads to the olefin (CCLXIV). The formation of the 6,9-epoxy-unit in compound (CCLXIV) takes place on treatment with toluene-*p*-sulphonyl chloride (pyridine, 40 °C) or methanesulphonyl chloride ($Et_3N$, $CH_2Cl_2$, −78 °C). The conversion of compound (CCLXV) into (6*S*)-$\Delta^7$-$PGI_1$ (CCLXIX) is carried out in four stages: (1) hydroboration of compound (CCLXV) and 9-BBN and subsequent oxidation afford the primary alcohol (CCLXVI); (2) treatment of compound (CCLXVI) with 10% $H_2O_2$ results in the formation of the unsaturated compound (CCLXVII); (3) mild acid hydrolysis of compound (CCLXVII) leads to the C(1) alcohol (CCLXVIII); (4) selective oxidation of compound (CCLXVIII) over $Pt/O_2$ produces compound (CCLXIX) (Scheme 23).

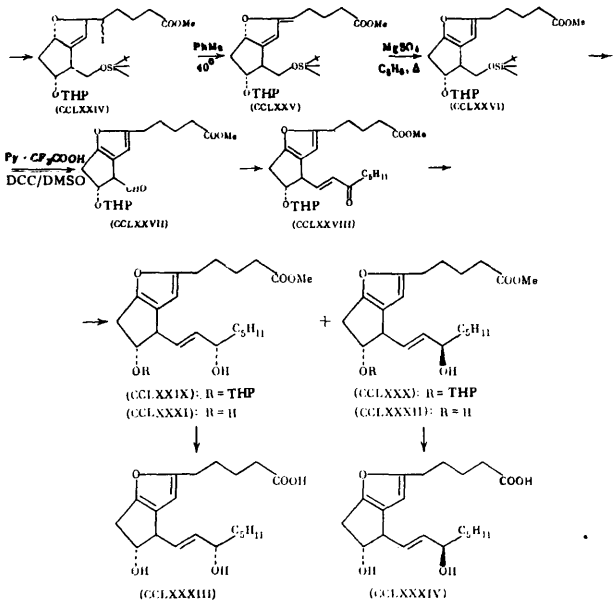
Scheme 23



Stable PC analogues having a furan ring instead of the enolic ether group have been synthesised.[75] The introduction of the phenylseleno-group in the α-position in the lactone (CCLXX) followed by treatment with $(MeSi)_2NLi$ and PhSeCl (THF), −70 °C, the elimination of the phenylseleno-group under oxidation conditions ($H_2O_2$), and the reintroduction of the phenylseleno-group ($NaHB_4$, PhSeSePh, EtOH) result in the formation of the β-phenylselenolactone (CCLXXI). The reduction of the latter with DIBAH (−70 °C), condensation with the lithium salt of 4-CBTP, and treatment of the resulting carboxylic acid with $CH_2N_2$ lead to the ester (CCLXII). The bicyclic iodoester (CCLXXIII) is obtained by treating compound (CCLXXII) with $I_2$ and $NaHCO_3$ with subsequent elimination of the phenylseleno-group and the formation of the dihydrofuran (CCLXXIV). The dehydroiodination of compound (CCLXXIV) with DBU gives rise to the very labile dienol ether (CCLXXV), which immediately isomerises to the furan derivative (CCLXXVI). The protecting group in compound (CCLXXVI) is removed with TBAF and the resulting alcohol is oxidised to the unstable aldehyde (CCLXXVII), which is condensed with dimethyl 2-oxoheptylphosphonate to form the enone (CCLXXVIII). The latter is reduced to $NaBH_4$ in the 15α- and 15β-alcohols (CCLXXIX) and (CCLXXX) (53% and 39% respectively). After removal of the THP protecting group in the usual way, the methyl esters (CCLXXXI) and (CCLXXXII) are obtained and then hydrolysed to the free acids (CCLXXXIII) and (CCLXXXIV) (Scheme 24).

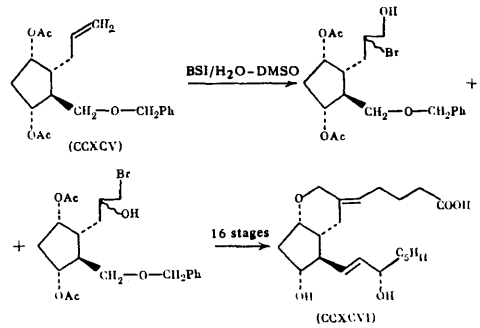
Scheme 24





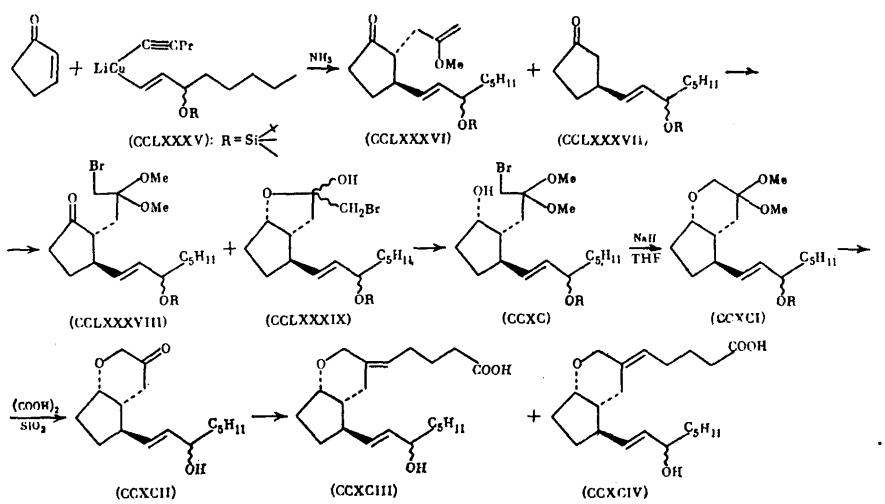
A synthesis of 11-deoxyhomo-PC analogues with a small number of stages has been proposed. The key stage in the synthesis is the reaction involving the coupled addition of organocuprate and alkylation of the resulting enolate.[76,77] Treatment of cyclopent-2-enone with the mixed cuprate (CCLXXXV) and alkylation of the intermediate enolate with 2-methoxyallyl bromide lead to a mixture of the alkylated product (CCLXXXVI) and the non-alkylated ketone (CCLXXXVII). Bromination of compound (CCLXXXVI) yields the α-bromoketal (CCLXXXVIII) together with the bicyclic acetal (CCLXXXIX). The stereospecific reduction of the keto-group in compound (CCLXXXVIII) with potassium *t*(*s*)-butylhydroborate leads to the α-alcohol (CCXC), which is cyclised to the ketal (CCXCI) with the simultaneous elimination of HBr. The hydrolysis and desilylation of compound (CCXCI) lead to the ketone (CCXCII), whose condensation with 4-CBTP gives rise to a mixture of compounds (CCXCIII) and (CCXCIV), which can be separated chromatographically (Scheme 25).

A similar approach to the synthesis of homo-PC (CCXCVI) is based on the use of the alkene (CCXCV). However, in the stage involving the addition of HOBr to the double bond, which precedes cyclisation, a low selectivity is observed:[78]

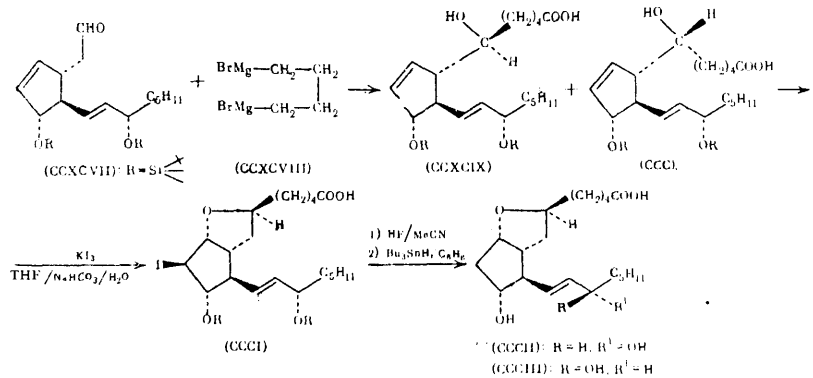


The stereoselective synthesis of the racemic 6β-$PGI_1$, which is a biologically active stable PC analogue, has been achieved.[79,80] The aldehyde (CCXCVII) reacts with an excess of the bis-Grignard reagent (CCXCVIII) and subsequent carboxylation with gaseous $CO_2$ affords a mixture of the acids (CCXCIX) (6α-OH) and (CCC) (6β-OH). When this mixture is treated with $KI_3$, the esters of 10β-iodo-derivative (CCCI) (34%) and the 6α-hydroxy-derivative (CCXCIX) (40%) are obtained. Compound (CCXCIX) is separated chromatographically, subjected to Collins oxidation, and then reduced with $NaBH_4$ to a mixture of compounds (CCXCIX) and (CCC), which is reused. When compound (CCCI) is treated with HF, (±)-6β-$PGI_1$ (CCCII) and (±)-6β-epi-$PGI_1$ (CCCIII) are obtained and are separated chromatographically (Scheme 26).

Scheme 25



Scheme 26

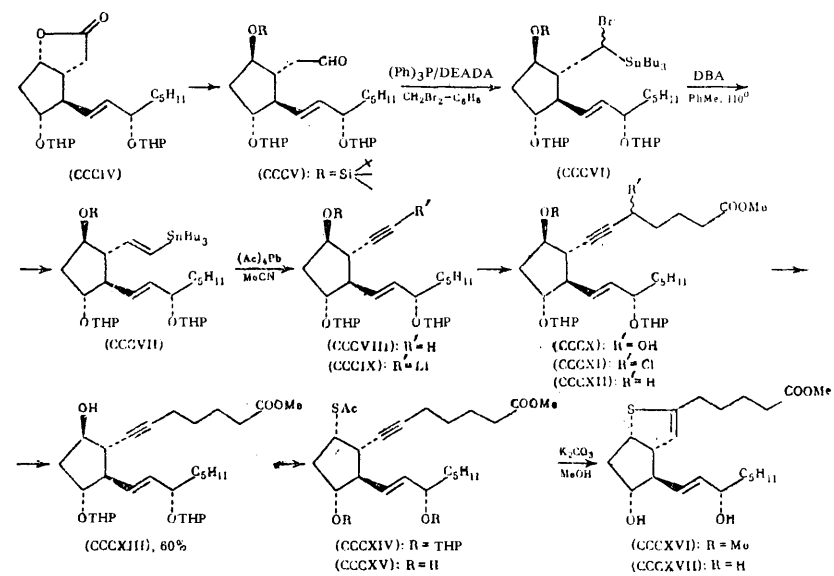


### 4. Prostacyclin Analogues From Which the O Atom in the 9-Position Has Been Replaced by Other Heteroatoms. Prostacyclin Analogues Containing Additional Heteroatoms

In order to elucidate the influence of the replacement of the O(9) atom by other heteroatoms, for example S and N, on the biological properties of PC, a series of syntheses were carried out, as a result of which it was possible to establish that the PC heteroanalogues exhibit a weaker biological activity than PC itself.[21,43]

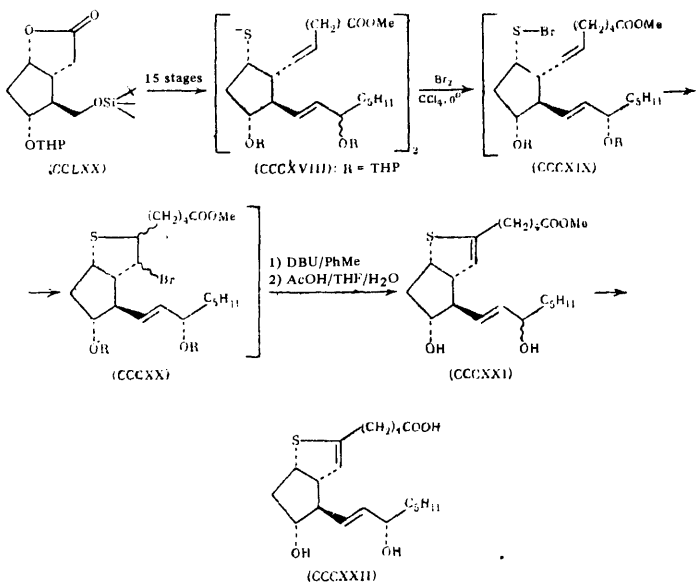
A new method for the conversion of the aldehyde into the acetylenic derivative via 1-alkenyltin was used in the synthesis of 9(*O*)-thia-$\Delta^6$-$PGI_1$ (CCCXVII).[81] The initial aldehyde (CCCV) was obtained from the well known lactone (CCCIV) in six stages (overall yield 57%). The aldehyde is converted in two stages into the α-bromoalkyltin derivative (CCCVI) (54%). The elimination of HBr from compound (CCCVI) gives rise to the vinyltin derivative (CCCVII) in a satisfactory yield. Further treatment of compound (CCCVII) leads to the terminal acetylene (CCCVIII) (63%). The condensation of the lithio-derivative (CCCIX) with methyl 4-formylbutanoate results in the formation of the propargyl alcohol (CCCX). The replacement of the OH group in compound (CCCX) by chlorine leads to compound (CCCXI), whose subsequent treatment with tri-n-butyltin hydride affords the propargyl chloride (CCCXII). After the removal of the protecting group in compound (CCCXII), the 9β-alcohol (CCCXIII) is formed and is then converted into the 9α-thia-acetate (CCCXIV) by Volante's method [$(C_6H_5)_3P$/di-isopropyl azodicarboxylate in the presence of thioloacetic acid]. The removal of the THP group in compound (CCCXIV) yields compound (CCCXV) (83%), the subsequent hydrolysis of which gives rise to the dihydrothiophen derivative (CCCXVI) (endoenol, 66%). Alkaline hydrolysis of compound (CCCXVI) with LiOH in a THF–$H_2O$ mixture followed by the adjustment of the pH to 4.01 with the aid of a buffer solution leads to compound (CCCXVII) (Scheme 27).

Scheme 27

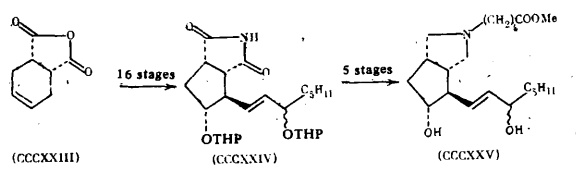


The synthesis of the chemically stable 9(O)-thia-$\Delta^6$-PC (CCCXXII) from Corey's lactone (CCLXX), which is converted in the usual way into the disulphide (CCCXVIII), has been described. The bromination of compound (CCCXVIII), treatment with DBA, and the removal of protecting groups lead to different amounts of the methyl esters of compound (CCCXXI) and its 15-epimer. The conversion of the disulphide (CCCXVIII) into the sulphenyl bromide (CCCXIX) initiates a new intermolecular rearrangement with formation of the halogenotetrahydrothiophen derivative (CCCXX). Alkaline hydrolysis of compound (CCCXXI) affords compound (CCCXXII), which exhibits a high activity in the inhibition of the aggregation of platelets, comparable to the activity of 9(O)-thia-PC [82] (Scheme 28).

Scheme 28

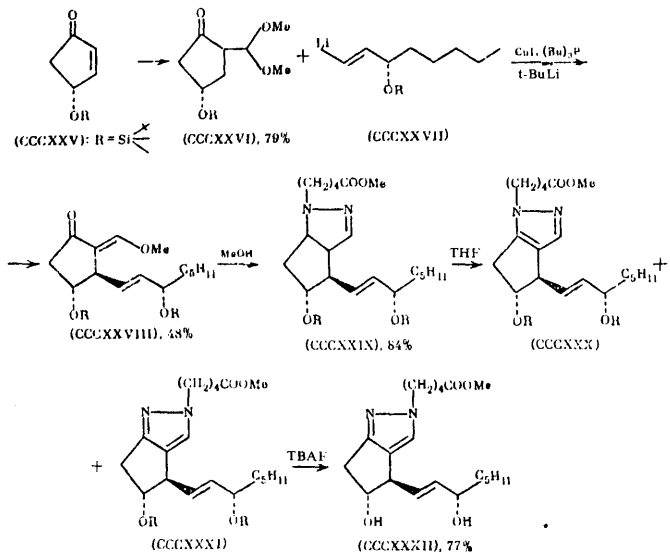



A multistage synthesis of racemic 6-aza-6,9-methano-$PGI_2$ (CCCXXV), which inhibits the aggregation of platelets, has been achieved. The anhydride (CCCXXIII) served as the starting material. It is converted into the imide (CCCXXIV) in 16 stages and the 6-aza-PC analogue (CCCXXV) was obtained from the latter in 5 stages: [83]




A convergent approach to the chiral analogue of the heteroaromatic PC has been proposed. [84] The enone (CCCXXV) is initially converted into the dimethoxymethyl derivative (CCCXXVI): treatment with (1) phenylselenotrimethylsilane and trimethylsilyltrifluoromethanesulphonate, (2) trimethyl orthoformate, (3) pyridine, and (4) 30% $H_2O_2$. The reaction of compound (CCCXXVI) with the organocuprate reagent obtained from copper(I) iodide and the lithium derivative (CCCXXVII) gives rise to the product (CCCXXVIII). Its condensation with hydrazine hydrate affords the pyrazole derivative (CCCXXIX), whose potassium salt is treated with methyl 5-iodopentanoate, which leads to a 1 : 1 mixture of the products (CCCXXX) and (CCCXXXI) (67%). After the removal of the protecting groups in compound (CCCXXXI), compound (CCCXXXII) is obtained (Scheme 29).

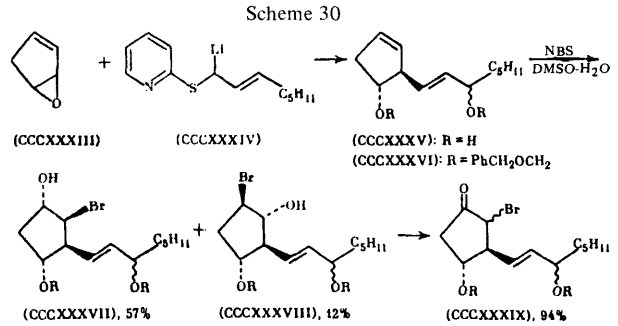
Scheme 29

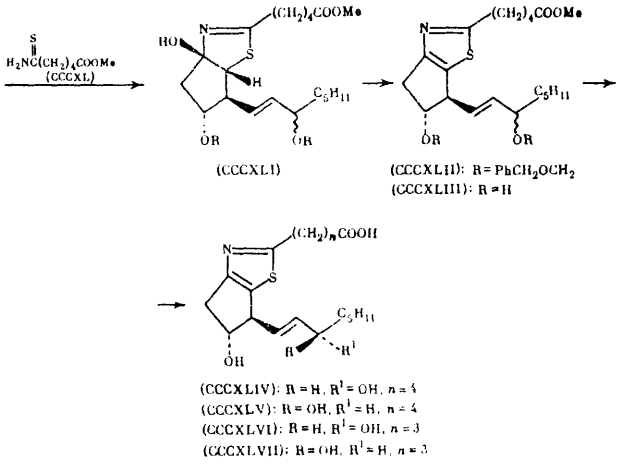



Thiazole analogues of PC are obtained from compound (CCCXXV), synthesised in several stages by the opening of the epoxy-ring in the 3,4-epoxycyclopentene (CCCXXXIII) by treatment with the lithio-derivative (CCCXXXIV). [85] The hydroxy-groups in the diol (CCCXXXV) are protected in the form of the bisbenzyloxymethyl ethers (CCCXXXVI), which give rise to an appreciable steric hindrance to electrophilic attack on the double bond in the side chain.

Treatment of compound (CCCXXXVI) with NBS gives rise to a mixture of two readily separated bromohydrins (CCCXXXVII) and (CCCXXXVIII). Oxidation of the main bromohydrin (CCCXXXVII) with pyridinium chlorochromate yields the bromoketone (CCCXXXIX) in the form of a mixture of epimers at C(8). The reaction of compound (CCCXXXIX) with the thioamide (CCCXL) leads to the hydroxythiazoline (CCCXLI), which is treated, without being isolated, with the complex of $(C_6H_5)_3P$ and DEADA, to give the thiazole (CCCXLII). After the removal of the protecting groups in compound (CCCXLII) and alkaline hydrolysis of the diol (CCCXLIII), the PC analogue (CCCXLIV) and its 15-epimer (CCCXLV) are obtained and are separated chromatographically. The nor-PC analogue (CCCXLVI) and its 15-epimer (CCCXLVII) are obtained analogously from the bromoketone (CCCXXXIX) and a thiazole derivative obtained from the methyl ester of glutaric acid monoamide (Scheme 30).

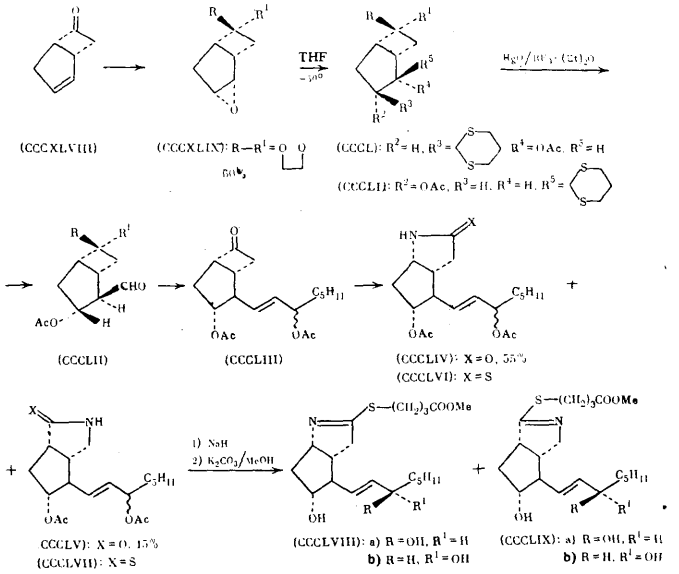
Scheme 30



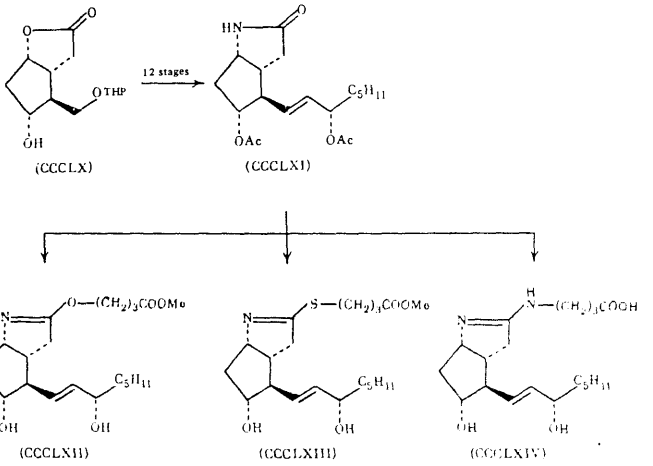



The synthesis of β-thiaimino-PC using bicyclo[3.2.0]hept-2-en-6-one (CCCXLVIII), the intermediate in the synthesis of natural PG, as the starting material has been described.[86] The ketone (CCCXLVIII) is converted by a standard method into the ketal (CCCXLIX) whose treatment with 2-lithiodithiane followed by acylation gives rise to the crystalline acetates (CCCL) and (CCCLI) (2 : 8, 61%), which are readily separated by crystallisation. Selective hydrolysis of the dithiane unit in the acetate (CCCLI) results in the formation of the aldehyde (CCCLII), whose condensation with the corresponding phosphonate, the reduction of the enone produced ($ZnBH_4$, diglyme), acylation, and the removal of the ketal protecting group lead to the ketone (CCCLIII). Treatment of compound (CCCLIII) with *o*-mesitylenesulphonylhydroxylamine yields the crystalline lactam (CCCLIV) and the isomeric lactam (CCCLV). On heating the mixture of lactams ($P_4S_{10}$.Py, toluene), the mixture of the thiolactams (CCCLVI) and (CCCLVII) is obtained (80%), whose alkylation with ethyl γ-bromobutyrate followed by the hydrolysis of the acetate groups affords a mixture of compounds (CCCLVIIIa, b) and (CCCLIXa, b) in an overall yield of 64%, which can be readily separated chromatographically (Scheme 31).

Scheme 31

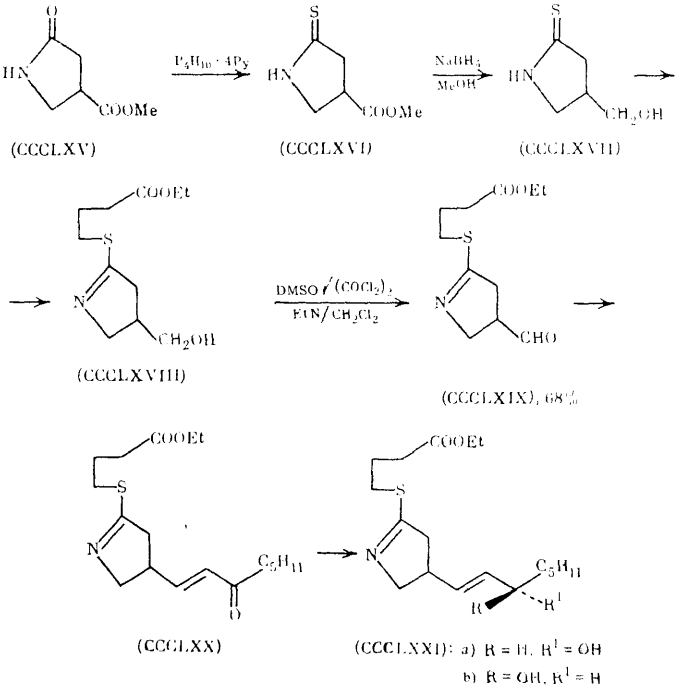



The lactone (CCCLX) can be converted into the lactam (CCCLXI), which is the key synthone in the synthesis of 4-oxa-9-aza-$PGI_1$ (CCCLXII), 4-thia-9-aza-$PGI_1$ (CCCLXIII), and 4,9-diaza-$PGI_1$ (CCCLXIV).[87]



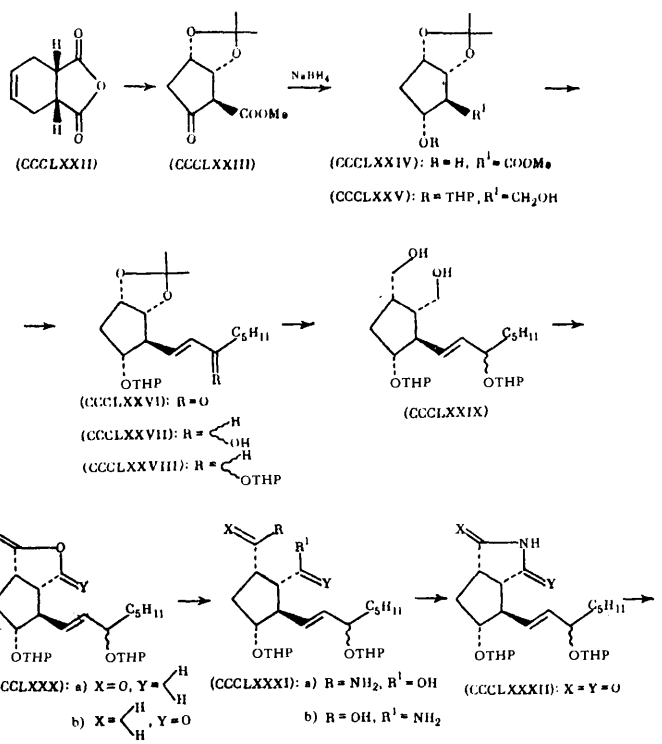

The racemic thiolactam esters (CCCLXXIa, b) are obtained from 4-methoxypyrrolidin-2-one (CCCLXV) via compound (CCCLXVI) and *S*-alkylation of the thiolactam alcohol (CCCLXVII) with ethyl ω-bromobutyrate to the thiaimino-alcohol (CCCLXVIII). After the oxidation of the OH group in compound (CCCLXVIII), the aldehyde (CCCLXIX) is obtained and its condensation with dimethyl 2-oxoheptylphosphonate leads to the enone (CCCLXX). The reduction of the last compound with diisobornyloxyaluminium isopropoxide yields a 1 : 1 mixture of the epimers (CCCLXXIa, b) which can be separated chromatographically (Scheme 32).[88]

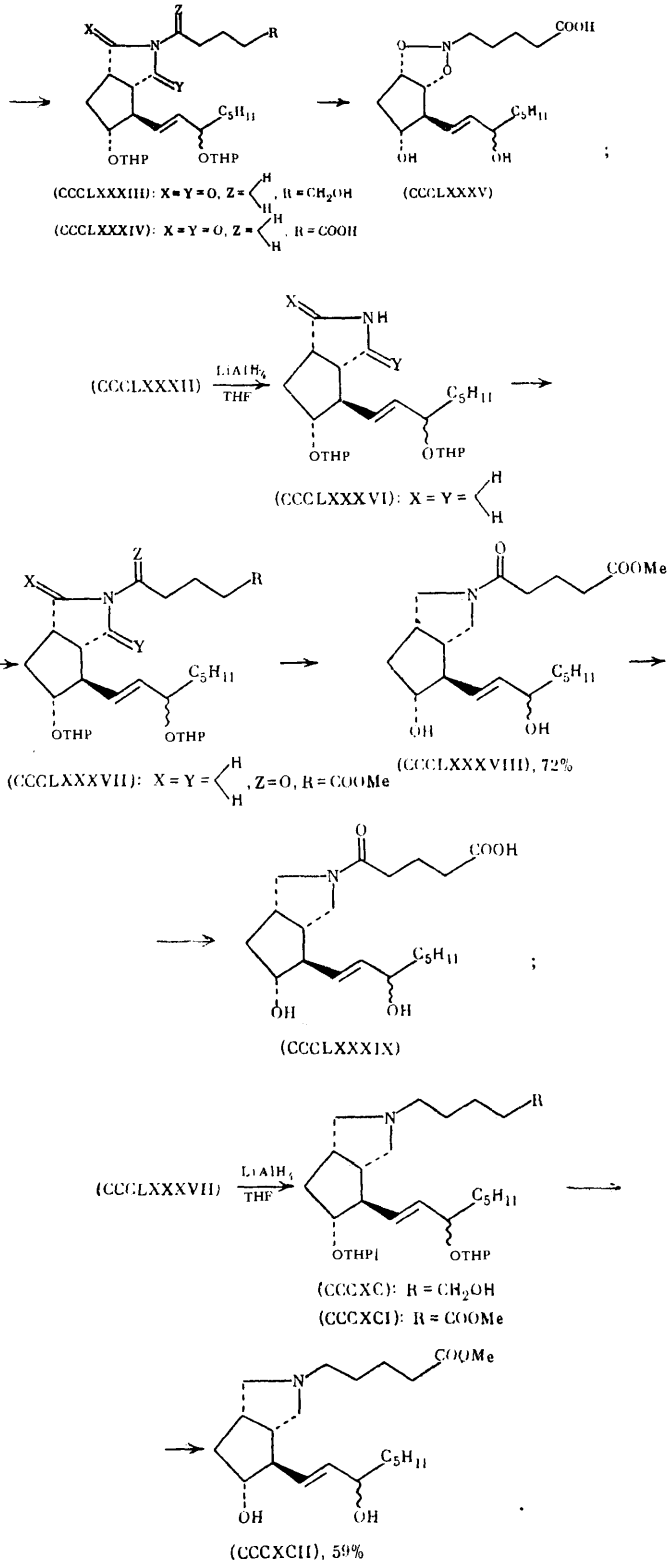
Scheme 32



The synthesis of analogues of *dl*-6-aza-6,9-methano-$PGI_1$ (CCCLXXXV), (CCCLXXXVIII), (CCCLXXXIX), and (CCCXCII) from the anhydride (CCCLXXII), which is converted in 5 stages into the β-ketoester (CCCLXXIII), has been achieved.[89] Reduction of the keto-group makes it possible to obtain compound (CCCLXXIV). By protecting the OH group in compound (CCCLXXIV) and reducing the ester group with DIBAH, one can obtain the alcohol (CCCLXXV), whose oxidation to the aldehyde and subsequent condensation with dimethyl 2-oxoheptylphosphonate give rise to the enone (CCCLXXVI). The reduction of the keto-group in compound (CCCLXXVI) with $NaBH_4$ leads to a mixture of the C(15)-epimers (CCCLXXVII), which is converted, without being isolated, into compound (CCCLXXVIII) and the latter is converted into the diol (CCCLXXIX) by reaction with pyridinium toluene-*p*-sulphonate. The Sarett oxidation of compound (CCCLXXIX) leads to a mixture of two isomeric γ-lactones (CCCLXXXa, b), b) (94%) and their treatment with hydrazine results in the formation of a mixture of the amidoalcohols (CCCLXXXIa, b), whose oxidation gives rise to the imide (CCCLXXXII). The reaction of the imide with 5-aminopentanol leads to the imidoalcohol (CCCLXXXIII), the Sarett oxidation of which affords the imidoacid (CCCLXXXIV). After the removal of the protecting groups in compound (CCCLXXXIV), compound (CCCLXXXV) is obtained. The reduction of compound (CCCLXXXII) leads to the formation of the cyclic amine (CCCLXXXVI), which is converted into the amidoester (CCCLXXXVII) after treatment with glutaric anhydride and esterification with $CH_2N_2$. The removal of the protecting groups in compound (CCCLXXXVII) affords compound (CCCLXXXVIII), whose alkaline hydrolysis leads to compound (CCCLXXXIX). The reduction of compound (CCCLXXXVII) leads to the formation of the aminoalcohol (CCCXC). It is successively oxidised by the Jones' method and esterified with $CH_2N_2$ to the aminoester (CCCXCI) and, after the removal of the protecting groups in the latter, compound (CCCXCII) is obtained (Scheme 33).

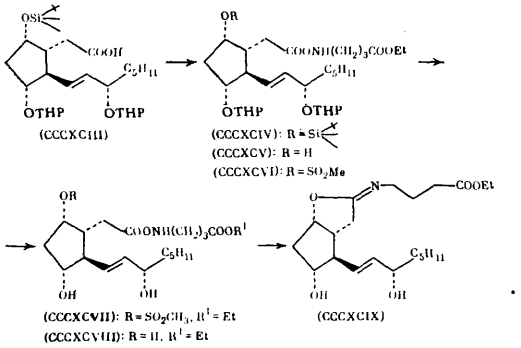
Scheme 33



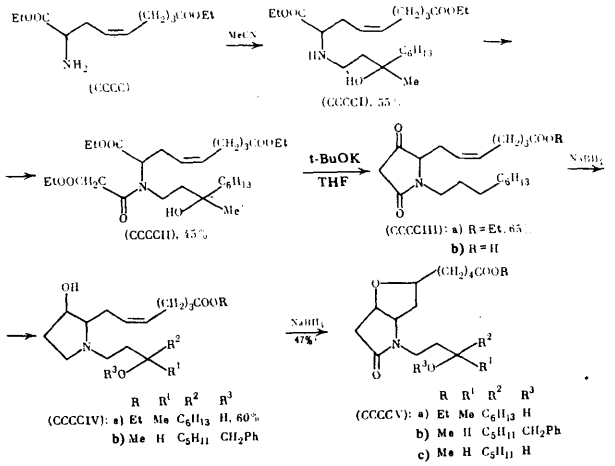

The synthesis of the optically active 5-aza-PC derivative (CCCXCIX) in which the enol ether unit has been replaced by the iminoether system has been described.[90-92] The acid (CCCXCIII) is first converted into a mixture of anhydrides

and the latter are converted by reaction with ethyl 4-aminobutanoate into the amine (CCCXCIV), whose reaction with TBAF produces the alcohol (CCCXCV). Subsequent removal of the protecting groups in the latter leads to the crystalline compound (CCCXCVII) (81%). The interaction of this compound with LiBr ($NaHCO_3$, DMF) leads to a mixture of compounds (CCCXCIX) and (CCCXCVIII), whose separation is the most important stage. Compound (CCCXCVIII) (30%) is isolated from the organic layer by partition between 0.1 *N* citrate buffer (pH 4) and the 4 : 1 ether-dichloroethane mixture. The crystalline compound (CCCXCIX) (51%) is isolated from the aqueous layer by treatment with $Na_2CO_3$ (pH 8) and extraction with $CH_2Cl_2$:



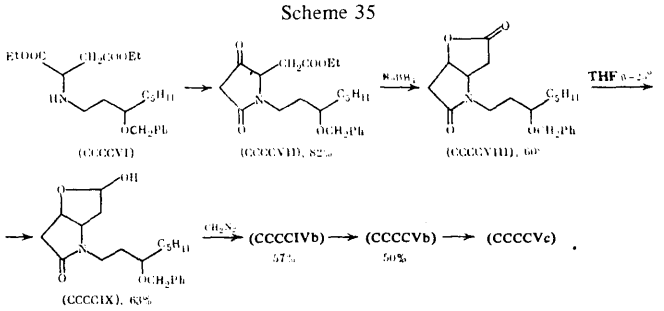
Analogues of 12-aza-PC can be obtained in two ways.[93] The first approach (Scheme 34) is based on the use of the amine (CCCC), whose treatment with 3-methyl-1-(toluene-*p*-sulphonyloxy)nonan-3-ol leads to compound (CCCCI), whose acylation with monoethyl malonate yields compound (CCCCII). The cyclisation of the latter to (CCCCIIIa) and treatment with anhydrous $MgSO_4$ afford compound (CCCCIIIb). Its reduction and treatment of compound (CCCCIVa) with mercury trifluoroacetate followed by reduction make it possible to obtain the 12-aza-PC analogue (CCCCVa).

Scheme 34



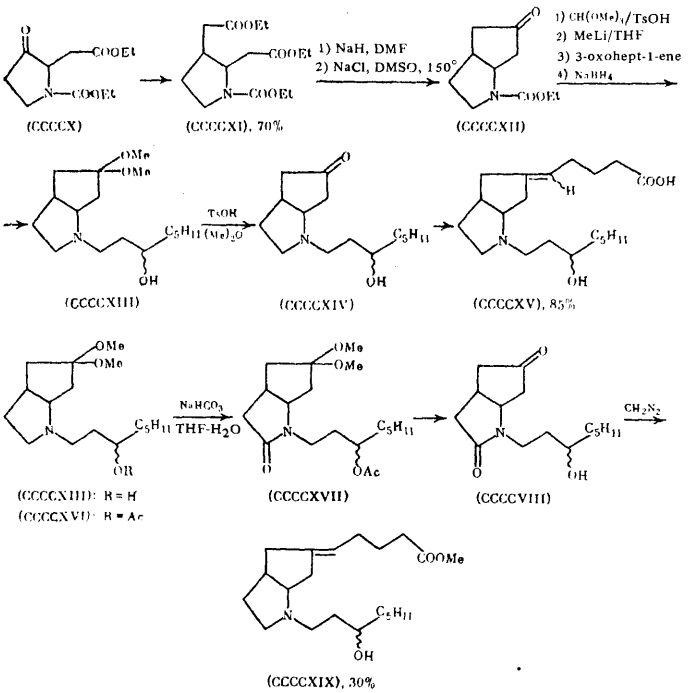
The second approach (Scheme 35) involves the application of the amine (CCCCVI), which is cyclised by the method described above. The potassium salt (CCCCVII) is reduced *in situ* to the bicyclic lactone (CCCCVIII). Its treatment with lithium tri-t-butoxyhydroaluminate leads to the lactol (CCCCIX), whose condensation with 4-CBTP and esterification give rise to compound (CCCIVb). The cyclisation of the latter to compound (CCCCVb) and hydrogenolysis over Pd/C result in the formation of the 12-aza-PC analogue (CCCCVc).

Scheme 35



In the search for anticlotting agents, the 12-azacarba-PC analogues (CCCCXV) and (CCCCXIX) have been synthesised from the common intermediate (CCCCXIII) (Scheme 36).[94] By reaction with $(MeO)_2OPCHNaCOOMe$ and subsequent hydrogenation, compound (CCCCX) is converted into the triester (CCCCXI), which is subjected to Dieckmann cyclisation and decarboxylation to give compound (CCCCXII). The ketone (CCCCXII) is converted into the dimethyl ketal (CCCCXIII) in four stages (overall yield 57%). After the removal of the protecting group in compound (CCCCXIII), the ketone (CCCCXIV) is obtained and condensed with 4-CBTP to form compound (CCCCXV). The intermediates in the synthesis of compound (CCCCXV), necessary for the conversion of the pyrrolidinone ring into a five-membered lactam, are used to synthesise the analogue (CCCCXIX). By protecting the OH group in compound (CCCCXIII) and by oxidising compound (CCCCXVI) with NBS, we obtain the 3-oxo-derivative (CCCCXVII). After the removal of the protecting groups, the hydroxy-ketone (CCCCXVIII) is condensed with the phosphorane to obtain an acid, whose subsequent esterification leads to compound (CCCCXIX).

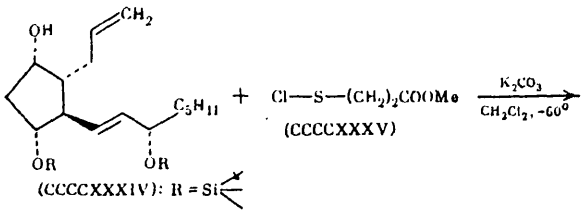
Scheme 36



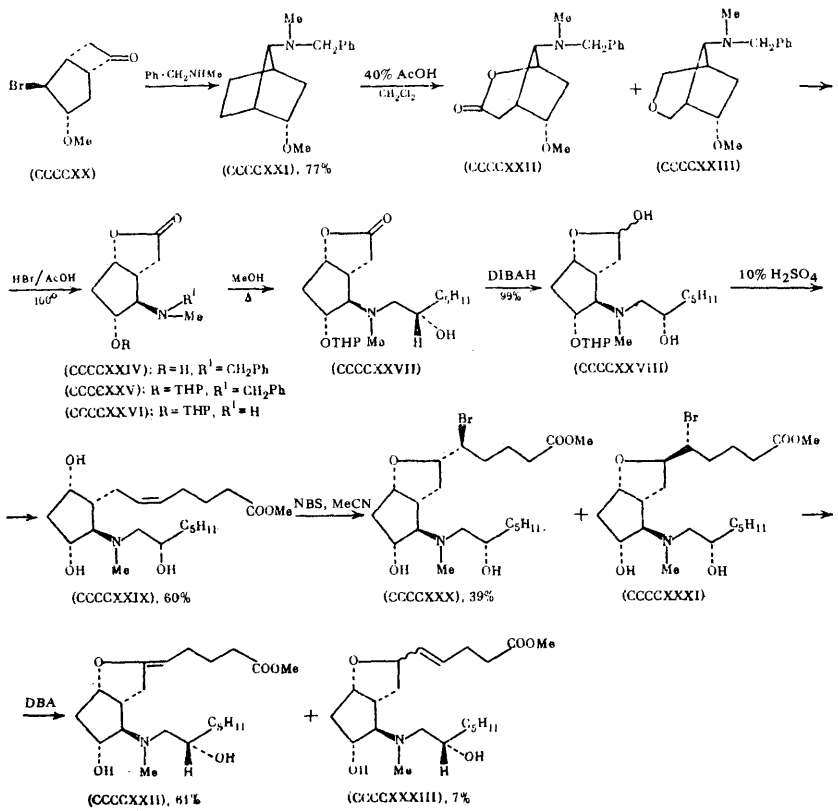
The stereoselective synthesis of the methyl ester of 13-aza-PC in 10 stages from the readily available 2-*exo*-bromo-3-*endo*-methoxybicyclo[3.2.0]heptan-6-one (CCCCXX) has been described.[95] The heptanone is converted into compound (CCCCXXI) and subjected to Baeyer–Villiger oxidation to give a mixture of the isomeric lactones (CCCCXXII) and (CCCCXXIII). The lactone (CCCCXXII) is kept in a mixture of acids, whereupon the methyl ester is cleaved with the simultaneous rearrangement of the δ-lactone to the γ-lactone (CCCCXXIV) (69%). Compound (CCCCXXIV) is converted via its hydroxy-group into the protected lactone (CCCCXXV). It is then hydrogenated over a Pd catalyst to the secondary amine (CCCCXXVI). The introduction of a ω-chain into this amine is achieved by reaction with (*S*)-pentyl oxide. The reduction of the lactone (CCCCXXVII) to the lactol (CCCCXXVIII), its subsequent condensation with 4-CBTP, and the removal of the protecting groups gives rise to the triol (CCCCXXIX). The hydrochloride of the latter is converted into the bromoesters (CCCCXXX) and (CCCCXXXI) (*endo* : *exo* = 3 : 1, 39%). Dehydrohalogenation of the two isomers after chromatographic separation leads to the methyl ester (CCCCXXXII) and its (4*E*)-isomer (CCCCXXXIII) (Scheme 37).

The addition of the alkanesulphonyl chloride (CCCCXXXV) to the alcohol (CCCCXXXIV) at −60 °C produces the bicyclic thiaesters (CCCCXXXVI) and (CCCCXXXVII). These diaesteroisomers are separated chromatographically and are converted, after the removal of the protecting groups and hydrolysis, into the 4-thia-PCI$_1$ analogues (CCCCXXXVIII) and (CCCCXXXIX) (Scheme 38).[96]

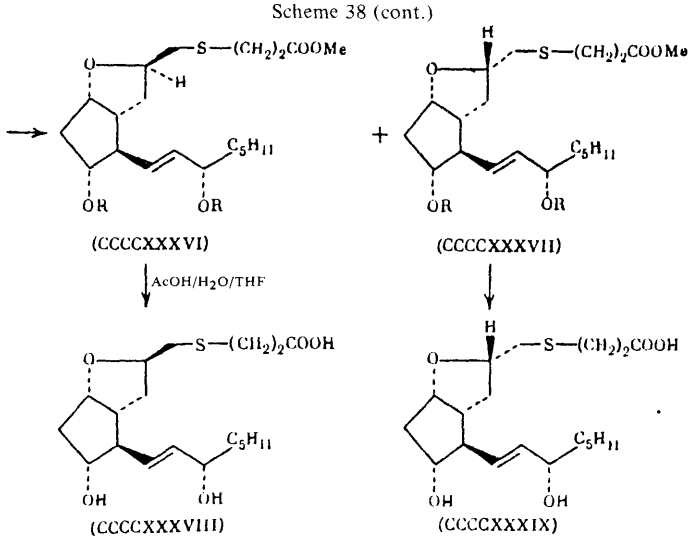
Scheme 38




Scheme 37



Scheme 38 (cont.)




After the review had been prepared for publication, a number of communications on the subject were published. Thus a new method for the construction of the ω-chain, with a stereospecific introduction of the 15α-hydroxy-group, was used in the synthesis of (±)-6,9α-methano-$PGI_3$.[97,98] Corey obtained a satisfactory yield of CC by an intramolecular thermal ene reaction.[99] The synthesis of CC from the key compound 2-(formylmethyl)-1-methylcyclopentane using a rhodium(I) complex has been achieved.[100] A new version of the synthesis of (+)-isocarbacyclin from a chiral substituted Corey's lactone has been developed.[101] In order to investigate biological activity, 6α-carba-$PGI_3$ has been synthesised from (1*S*,2*R*,3*R*,5*R*)-7,7-ethylenedioxy-2-formyl-3-tetrahydropyranyloxybicyclo[3.3.0]octane.[102] A method has been proposed for the synthesis of 13-thia-CC.[103] Cyanocarbacyclins have been synthesised using the stereospecific 1,4-hydrogenation of the corresponding conjugated dienes catalysed by the $ArCr(CO)_3$ complex as the key stage.[104] In the search for new stable and active PC analogues, (5*E*)- and (5*Z*)-(±)-CC were synthesised from cyclopent-2-en-1-one.[105] A synthesis of native (+)-9(*O*)-methano-PC from racemic (1*S**,5*R**)-7,7-ethylenedioxy-3-oxobicyclo[3.3.0]octane has been developed.[106] A simple synthesis of 13,14-didehydro-6,9α-methano-PC via the ethylene ketal of 3-oxotricyclo[$4.3.0.0^{2,4}$]nonan-8-one has been described.[107] A new CC analogue, namely 4,4,5,5-tetradehydro-9(*O*)-methane-$\Delta^{6(9\alpha)}$-$PGI_1$, has been synthesised using the regiocontrolled opening of the β-propyl-lactone ring by reaction with dialkylaluminium acetimide as the key stage.[108] A new synthesis of (+)-6α-CC from *cis*-bicyclo[3.3.0]octane-3,7-dione has been proposed.[109] The methyl ester of (±)-$PGI_2$ and its 15-epimer have been synthesised from 2-(cyclopent-2-enyl)-1-(2-oxocyclopentyl)ethanol.[110] In view of the interest in the antineoplastic properties of PC, the methyl ester of 12,13-didehydro-PC has been synthesised from 7-chloronorbornadiene.[111] A new synthesis of racemic 4-oxo-PC from 7-*endo*-t-butyldimethoxy-6-*exo*[3′(*S**)-butyldimethoxyoct-1′(*E*)-enyl]-3-oxo-2-oxabicyclo[3.3.0]octane† has been described.[112] Synthetic schemes have been devised for imidazoline, furan, thiophen, and pyrrole PC analogues.[113,114]

† The amended name of this compound is tentative since the original authors do not give it a name. The Russian text reads ...7-*endo*-*t*-butyldimethyloxy(BDMS)-6-*exo*-[3′(*S**).(BDMS-oxy)oct-1′(*E*)-enyl]-3-oxo-2-oxabicyclo[3.3.0]-octane [112] [Ed.of Translation].

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# Nucleophilic Substitution in β-Heterofunctional αβ-Unsaturated Iminium Salts

V.A.Usov, L.V.Timokhina, and M.G.Voronkov

Data on the hydrolysis, aminolysis, hydrothiolysis, and cyanolysis of β-heterofunctional αβ-unsaturated aliphatic and cyclic iminium salts are described systematically and surveyed. The direction of attack by the nucleophile on the two C-electrophilic centres in these compounds is discussed.
The bibliography includes 81 references.

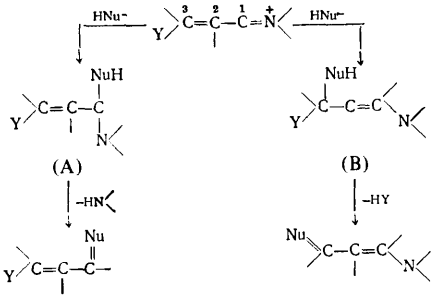
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## I. INTRODUCTION

The many-faceted and high reactivity of compounds containing the $Y-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=\overset{+}{N}\diagdown$ (Y = HO, RO, SH, or Hal) group is of considerable theoretical and practical interest. However, there have been as yet no monographs or reviews devoted to the chemistry of such compounds. There exist only individual publications surveying the methods of synthesis and the properties of certain representatives of this class of substances [Freimanis[1] (p.183) and Liebscher and Hartmann[2]]. This review deals with the available few synthetic studies involving the nucleophilic substitution in β-heterofunctional αβ-unsaturated iminium salts, certain theoretical aspects of these reactions are discussed (in so far as this is allowed by the data obtained), and an attempt is made to assess their preparative importance.

The nucleophilic substitution reactions in activated unsaturated systems proceed in most cases via an "addition–elimination" mechanism.[3-5] Thus, when a charged nucleophile interacts with the $Y-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=\overset{+}{N}\diagdown X^-$ group, two intermediate adducts, (A) or (B), can be formed depending on the direction of attack [on the C(1) or C(3) atom].



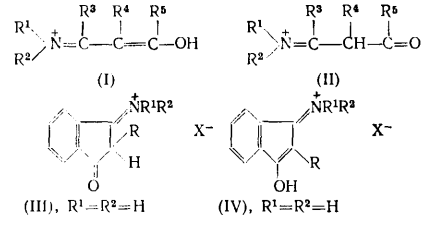
The outcome of the nucleophilic substitution in salts of the given type should apparently be subject to both charge and orbital control and the direction of the reaction should accordingly depend on the "hard–soft" properties of the nucleophile and both electrophilic centres in the substrate. Furthermore, in each specific case one must take into account the influence of the steric and electronic effects of the substituent in the pentad $Y-C(R^1)=C(R^2)-C(R^3)=\overset{+}{N}R^4R^5$, the acid–base properties of the medium, and the effects of solvation, temperature, and reaction time.

The first attempts to carry out calculations for the cations $Y-\overset{|}{C}=C-C=\overset{+}{N}\diagdown$ by the LCMO PPP method [Freimanis[1] (p.173) and Liebscher and Hartmann[2]] did not permit the elucidation of the specific reactivities of the C(1) and C(3) atoms. In only one investigation[6] was a more far-reaching quantum-mechanical analysis of nucleophilic substitution in 3-hetero-substituted cyclohex-2-ene-1-iminium salts carried out and a conclusion was reached about the preferred direction of the reactions of these salts with nucleophiles from the standpoint of the principle of "hard" and "soft" acids and bases (HSAB). The synthesis of certain new types of organic sulphur compounds became possible on the basis of these ideas.

## II. β-HYDROXY AND β-ALKOXY-IMINIUM SALTS

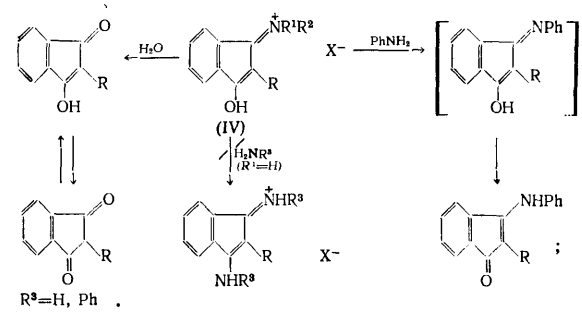
### 1. β-Hydroxyiminium salts

The reactivity of enaminoketones in nucleophilic substitution reactions is fairly low but increases appreciably in the presence of organic[7] or inorganic[8,9] acids. This can be explained by the intermediate formation in acidic media of the corresponding 3-hydroxyprop-2-eneiminium salts (I), which are highly electrophilic. Apart from protonation at the oxygen atom, there is a possibility of the C(2)-protonation with formation of the salt (II) [Freimanis[1] (p.187)]:



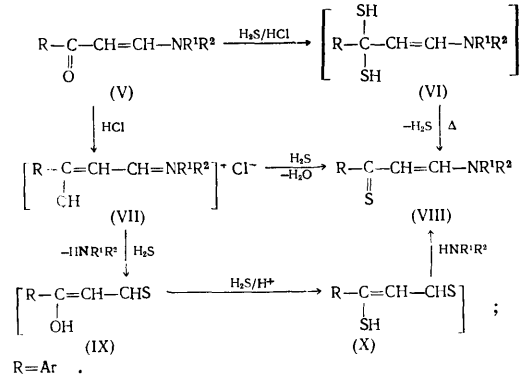
Precisely these two types of salts [compounds (III) and (IV)] were isolated among indene derivatives.[1] The form (III) is the most stable in the crystalline state. However, the reactions of enamines proceed as a rule in highly polar media, i.e. under conditions favourable for the existence of more polar tautomers—3-hydroxyind-2-eneiminium salts (IV).

Their behaviour has been investigated in hydrolysis and aminolysis reactions:[10]

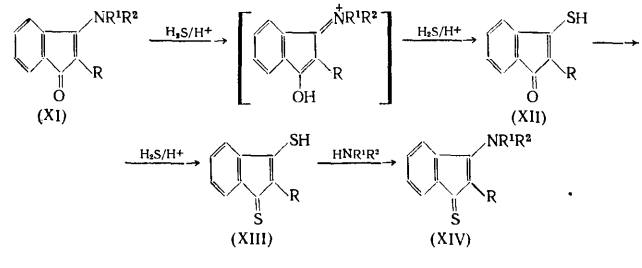


The preferred site of attack by the nucleophile in the salts (IV) is the $C=\overset{+}{N}$ bond. The explanation is that the solvated hydroxy-group is appreciably shielded and the nucleophilic species is directed towards the other electrophilic centre in the molecule.[10]

It has been suggested[1] that the hydrothiolysis of enaminoketones, which is usually carried out in alcoholic media in the presence of HCl, HF, or $H_2SO_4$, also proceeds via the intermediate hydroxypropeneiminium salt (VII). The second possible version of this reaction is believed to involve the intermediate formation of the *gem*-dithiol (VI).[11] Accordingly, the interaction of, for example, 1-aryl-3-(*NN*-dialkylamino)-1-propenones (V) with hydrogen sulphide in an alcoholic HCl solution[11–14] can be represented schematically as follows: (V) → (VI) → (VIII) and (V) → (VII) → (VIII).

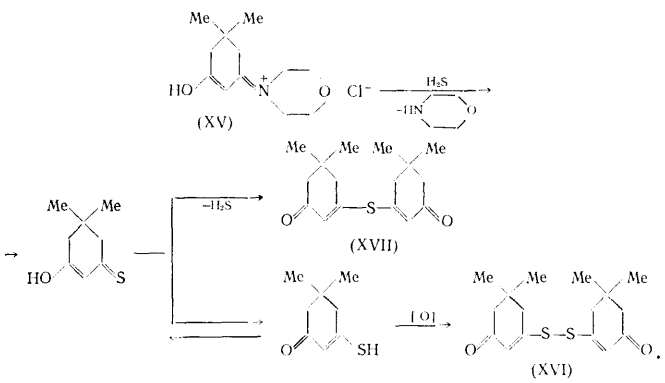


Bearing in mind the ability of various enaminoketones to form iminium salts with protic acids,[1,15,16] preference may be given to the intermediate (VII). However, the direct transformation (VII) → (VIII) is doubtful, since the reaction of 2-aryl-3-(*NN*-dialkylamino)-1-indenones (XI) with hydrogen sulphide in the presence of HCl in alcoholic media is accompanied by the thiolysis of the amino-group with formation of the mercaptoindenones (XII):[17]



Under the same conditions, compounds (XII) are converted into the β-dithiodiketones (XIII),[18] which readily react with highly basic amines to form the enaminothioketones (XIV).[19] For the same reason and also bearing in mind the mode of hydrothiolysis of the iminium salts,[6,20-23] one must postulate the more complex reaction scheme (V) → (VII) → (IX) → (X) → (VIII), which accounts for the low yield of the enaminothioketones (VIII) (3–10%).

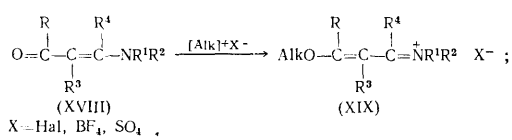
When 3-hydroxy-5,5-dimethylcyclohex-2-ene-1-*N*-morpholinium chloride (XV) reacts with hydrogen sulphide at −60 °C in dimethylformamide (DMF), the disulphide (XVI) and the sulphide (XVII) are present in the reaction mixture. Their formation indicates the attack by the nucleophile on the C=N̊ bond. The process probably proceeds in accordance with the mechanism[24]



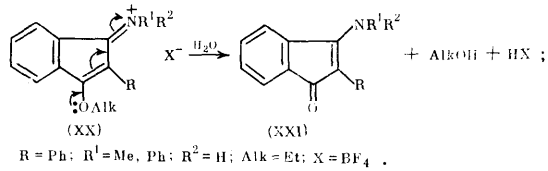
The benzeneiminium analogue of the salt (XV) does not react with hydrogen sulphide in the range from −60 °C to 15 °C, which indicates the low electrophilicity of this salt.

## 2. β-Alkoxyiminium Salts

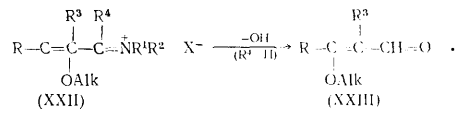
The salts (XIX) containing the β-alkoxypropeneiminium group are obtained by alkylating the corresponding enaminoketones (XVIII) by alkyl halides, dialkyl sulphates, or triethyloxonium tetrafluoroborate:[1]



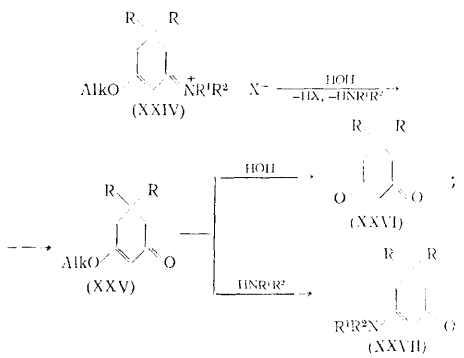
*Hydrolysis.* The salts containing the β-alkoxypropeneiminium group are much more sensitive to hydrolysis than the corresponding bases. Thus the tetrafluoroborates of 1-imino-3-ethoxyindenes (XX) are converted into the aminoindenones (XXI) even in the presence of traces of moisture.[25] The high lability of the salt (XX) can be explained by the increased electrophilicity of the C(3) atom in the cation induced by the strong electron-accepting effect of the iminium group. With increase of the latter, the stability of compounds (XX) falls. For example, the *N*-methyl-substituted salt (XX) initially dissolves in water and only then the enaminoketone (XXI) is formed. On the other hand, the *N*-phenyl-substituted compound (XX) is very hygroscopic and can be purified only in the form of the hydrolytically more stable free base:



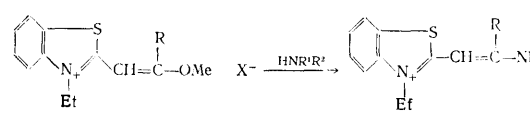
It was believed that salts of type (XX) are hydrolysed exclusively at the C(3)–O bond.[1] However, this is apparently true only for the hydrolysis of such compounds in neutral and acid media. Thus, when the salt (XXII) was treated with aqueous alkali, the aldehyde (XXIII), which is a product of the hydrolysis at the C(1) atom, was isolated:[26]



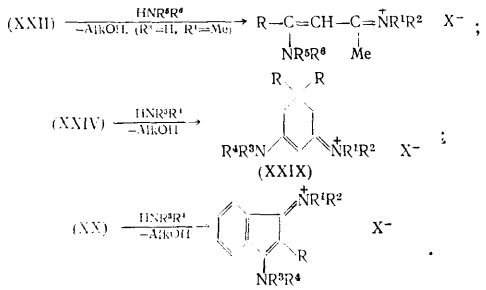
The hydrolysis of 3-alkoxycyclohex-2-ene-1-iminium salts (XXIV) in the presence of triethylamine at 20 °C also takes place at the C(1)=N̊ bond with elimination of amines and the formation of 3-alkoxycyclohex-2-en-1-ones (XXV).[27] After prolonged storage or heating of the reaction mixture, the product of further hydrolysis, namely the diketone (XXVI), and also the enaminoketone (XXVII) are formed. The latter is apparently obtained as a result of the reaction of the alkoxyketone (XXV) with the eliminated amine, which has been confirmed by the reaction of compound (XXV) with piperidine [the aminolysis of dimedone (XXVI) takes place under more severe conditions[28]]:



*Aminolysis.* The reactions of salts containing the β-alkoxypropeneiminium group with amines were first achieved for substituted benzothiazolium salts (XXVIII),[29] this being the only possible mode of reaction:



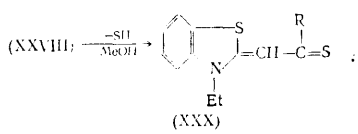
The aminolysis of other salts (aliphatic,[26,29] alicyclic,[23,28,30] and indene[31] salts) also takes place at the C(3)–O bond. These reactions are of great preparative importance for the synthesis of enaminoimines.[1] Other conditions being equal, the indene derivatives react more readily. This can be explained by the increased electrophilicity of the aryl substituent and hence by the greater reactivity of the C(3) atom. The reactions of aliphatic salts (XXII), the cyclohexene salts (XXIV), and the indene salts (XX) with 1,4-phenylenediamine in alcoholic media provide a clear example:[31]



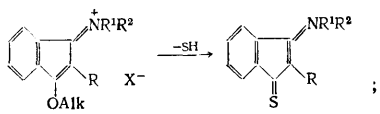
The rate of reaction depends on the basicity of the amine. Thus the reactions of *O*-alkyl derivatives of the cyclohexene enaminoketones (XXIV) with pyrrolidine in methanol take place instantaneously with evolution of heat and lead to the corresponding enaminoimine (XXIX) in a high yield (92%); the interaction of this salt with the less basic diethylamine is slow (48 h).[28]

In the aminolysis of salts with the 3-alkoxypropeneiminium group, the reaction involving the second electrophilic centre, namely the C(1) atom, was not observed. However, the overall data for the reactions of these compounds as well as their thio-analogues[32,33] with nucleophiles do not rule out the possibility of the amine exchange at the C(1) atom under certain conditions.

*Hydrothiolysis and alkanethiolysis.* When substituted benzothiazolium salts (XXVIII) react with alkali metal hydrogen sulphides, the alkoxy-group is readily substituted by the mercapto-group with formation of the enaminothioketones (XXX).[29] Subsequently this reaction became one of the preparative methods for the synthesis of enaminothioketones:

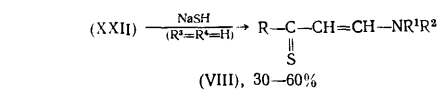


When 2-aryl-3-ethoxyindene-1-iminium tetrafluoroborates (XX) were heated with sodium hydrogen sulphide in methanol, a series of 3-amino-2-arylindene-1-thiones (XIV) were obtained.[34] The *N*-unsubstituted aminothioketones (XIVa–c) are formed in 55–74% yield. The yield of *N*-monoalkyl-substituted 3-amino-2-phenylindene-1-thiones (XIVe, f) is 31 to 38% and that of 2-phenyl-3-piperidinoindene-1-thione (XIVi) is below 30%. These data suggest that the reaction of the tetrafluoroborate (XX) and particularly that of the *NN*-disubstituted derivative (XXi) with sodium hydrogen sulphide can be determined to a large extent also by the attack of the *S*-nucleophile on the C=N bond with a subsequent wide range of different reactions:

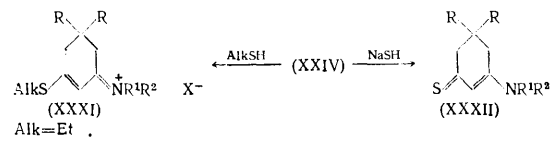


a) R=Ph, $R^1$=$R^2$=H; b) R=4-$MeOC_6H_4$, $R^1$=$R^2$=H; c) R=4-$ClC_6H_4$, $R^1$=$R^2$=H; d) R=1-$C_{10}H_7$, $R^1$=$R^2$=H; e) R=Ph, $R^1$=Me, $R^2$=H; f) R=Ph, $R^1$=$PhCH_2$, $R^2$=H; g) R=1-$C_{10}H_7$, $R^1$=Me, $R^2$=H; h) R=1-$C_{10}H_7$, $R^1$=$PhCH_2$, $R^2$=H; i) R=Ph, $R^1R^2$=$(CH_2)_5$;
Alk=Et; X=$BF_4$ .

The reactions of the salts (XXII) with sodium hydrogen sulphide are used to obtain aliphatic enaminothioketones (VIII):[35]



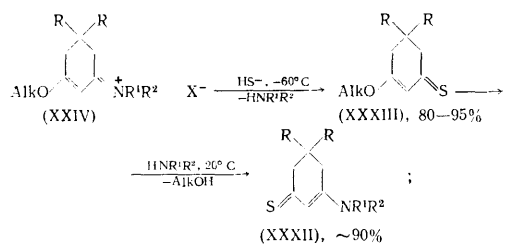
*N*-Monosubstituted 3-ethoxy-5,5-dimethylcyclohex-2-ene-1-iminium salts (XXIV, $R^1$ = H; $R^2$ = Me or Ph; X = $BF_4$) react with sodium hydrogen sulphide in absolute alcohol at 20 °C to form a complex mixture of sulphur compounds, the corresponding enaminothioketones (XXXII) being obtained in a low yield (~9%):[36]



Treatment of 3-ethoxy-5,5-dimethylcyclohex-2-ene-1-pyrrolidinium iodide [XXIV, $R^1R^2$ = $(CH_2)_4$; X = I] with ethanethiol in methanol in the presence of sodium methoxide at 25 °C led to a salt of the ethylthio-derivative (XXXI)† in 66% yield.[30]

In the instances of hydrothiolysis described above, the attack by the nucleophile on the C(3) atom in the propene fragment predominates. However, a recent systematic investigation of the hydrothiolysis of iminium salts with the cyclohexene skeleton led to a new idea about the mode of nucleophilic substitution in salts containing the 3-alkoxy-, 3-alkylthio-, and 3-chloropropeneiminium groups.[6,20–23] The results cast doubt on the apparently self-evident nature of the reaction of the $HS^-$ anion at the C(3) atom in the compounds investigated.

Thus the study of the interaction of 3-alkoxycyclohex-2-ene-1-iminium salts (XXIV) with hydrogen sulphide or metal hydrogen sulphide at a low temperature established that the conversion of the initial compound (XXIV) into the enaminothioketones (XXXII) is a two-stage process:[23]



R=H, Me; $R^1$=H, Alk, $-(CH_2)_n-$;
$R^2$=H, Alk, $-(CH_2)_n-$, Ar; X=$BF_4$, I .

The first stage, namely the hydrothiolysis of the C(1)=N bond and not the C(3)–O bond as was assumed previously, takes place at −60 to −40 °C and leads to previously unknown 3-alkoxycyclohex-2-ene-1-thiones (XXXIII) in a high yield. The second stage, namely the aminolysis of the stable intermediate (XXXIII), takes place at the C(3)–O bond and at 20 °C leads rapidly to a high yield of the enaminothioketones (XXXII).

The salts (XXIV) react with hydrogen sulphide only in a dipolar aprotic solvent [DMF, dimethyl sulphoxide (DMSO), hexamethylphosphoramide (HMP), and pyridine], known to

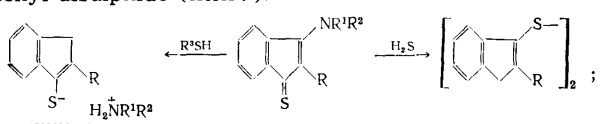
†One must bear in mind that the effective radius of the $EtS^-$ anion is much greater than that of the $HS^-$ anion[6] and that this may be responsible for the attack of the former on the sterically less hindered C–O bond.

be capable[37] of solvating the cations selectively and weakening the $H^+-{}^-SH$ bond, which increases the nucleophilicity of the hydrogen sulphide anion. Furthermore, the rate of nucleophilic substitution reactions is greatly influenced by the specific solvation of the anion.[38] The lower the degree of solvation of the anion, the higher its nucleophilicity and reactivity. Protic solvents solvate anions especially effectively owing to the tendency towards the formation of hydrogen bonds. In dipolar aprotic solvents the anions are less effectively solvated, i.e. here they behave as "true nucleophiles". In view of the necessary reaction temperature, a suitable solvent for the reaction (XXIV) → (XXXIII) is DMF.[6] The addition of a highly basic amine accelerates the process significantly and tends to increase the yield of the required product (XXXIII).

In a protic solvent (methanol, ethanol) the salts (XXIV) do not react with hydrogen sulphide at temperatures between −60° and 20 °C. When triethylamine or piperidine is added to the reaction mixture, only traces of compound (XXXIII) are formed. The salts (XXIV) react with sodium hydrogen sulphide in accordance with the scheme (XXIV) → (XXXIII) → (XXXII) both in DMF and in absolute methanol.[6,23]

At 20 °C, i.e. without the isolation of the intermediate (XXXIII), the reaction (XXIV) → (XXXII) terminates with a relatively low (~10%) yield of the enaminothioketone (XXXII). In this case the amine formed in the first stage is largely bound by the eliminated acid ($HBF_4$, $HClO_4$, HI) and hydrogen sulphide, which prevents the rapid occurrence of the subsequent reaction (XXXIII) → (XXXII).[6]

The reaction of 3-ethoxy-5,5-dimethylcyclohex-2-ene-1-*N*-piperidinium tetrafluoroborate [XXIV; R = Me; $R^1R^2$ = $(CH_2)_5$; Alk = Et; X = $BF_4$] with sodium hydrogen sulphide at 20 °C leads to the formation of a mixture of two thioketones (XXXII) and (XXXIII).[6,23] When the reaction is carried out in DMF at −60 °C with equimolar proportions of the initial compounds, the ethoxythioketone (XXXIII; Alk = Et) is formed preferentially, but, in the course of the treatment of the reaction mixture, it is almost fully converted into the enaminothioketone [XXXII; $R^1R^2$ = $(CH_2)_5$]. On the other hand, if acetic acid, which reduces the reactivity of piperidine, is added to the reaction mixture before this happens, it is possible to isolate the ethoxythione (XXXIII) in 54% yield. The yield of the enaminothioketone (XXXII) also depends on the competing reactions of compounds (XXXII) and (XXXIII) with *S*-nucleophiles. For example, the indene analogues (XIV) of compounds (XXXII) are readily reduced by thiols or hydrogen sulphide, forming the thiolates (XXXIV) [39] or bisindenyl disulphide (XXXV):[34]

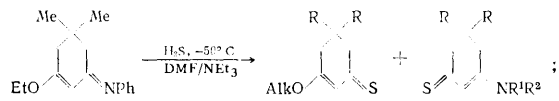


(XXXIV) (XIV) (XXXV)

R=Ph; $R^3$=Bu, Ph, H .

The multistage reaction (XXIV) → (XXXIII) → (XXXII) is followed by TLC and spectrometrically. For example, it has been found that, for R = OMe, $R^1R^2$ = $(CH_2)_2O(CH_2)_2$, $R^3$ = Me, and X = I, the above process is accompanied by the consecutive bathochromic and then hypsochromic shifts of the long-wavelength absorption band in the electronic spectrum—the colourless solution becomes raspberry-red and then yellow: $\lambda_{max}$ = 286 nm ($\lg\varepsilon$ = 3.8) → $\lambda_{max}$ = 498 nm ($\lg\varepsilon$ = 4.6) → $\lambda_{max}$ = 386 nm ($\lg\varepsilon$ = 4.4).[6]

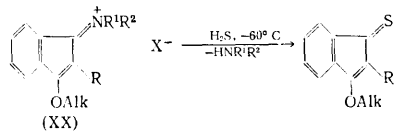
It must be emphasised that the hydrothiolysis of only the *NN*-disubstituted iminium salts (XXIV) at a low temperature leads exclusively to compounds (XXXIII).[6] The *N*-monosubstituted salts (XXIV) react with hydrogen sulphide in DMF in the presence of triethylamine to form a mixture of products containing small amounts of the alkoxythioketone (XXXIII) and the corresponding enaminothioketone (XXXII). This can be explained by the fact that in basic media the *N*-monosubstituted salts (XXIV) are deprotonated and are readily converted into the less reactive bases with the RO−C=C−C=N− group. Their hydrothiolysis can take place at the C(1) and (or) C(3) atoms[1] and should require more severe conditions. Thus a long time is required for the completion of the reaction of 3-ethoxy-5,5-dimethyl-1-phenylcyclohex-2-ene (XXXVI) with hydrogen sulphide; ultimately a mixture of products containing the ethoxythioketone (XXXIII) and the N-phenyleneaminothioketone (XXXII) is formed:[23]



(XXXVI) (XXXIII) (XXXII)

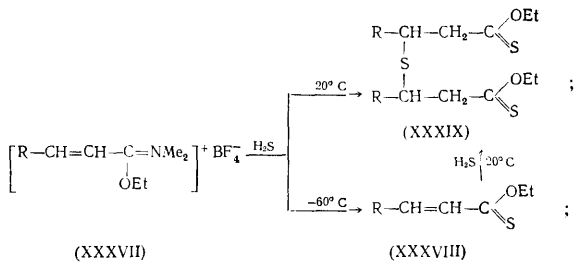
R=Me, $R^1$=H, $R^2$=Ph, Alk=Et .

The results of the hydrothiolysis of the cyclohexeneiminium salts (XXIV) have been confirmed in relation to the indene compond (XX):[40]



(XX)

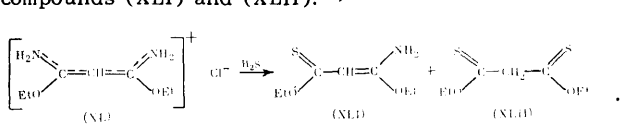
The hydrothiolysis of 1-alkoxyprop-2-eneiminium salts (XXXVII), the structural isomers of substituted cyclohexenes (XXIV), which takes place at −15 °C in a mixture of anhydrous ether and pyridine, is remarkable from this point of view. This reaction proceeds with elimination of the amine and retention of the C−O bond. Whereas at −60 °C the hydrothiolysis of the salt (XXXVII; R = Me) leads to compound (XXXVIII), the sulphide (XXXIX) was isolated at 20 °C. The latter is formed as a result of the addition of hydrogen sulphide to the C=C bond and subsequent intermolecular condensation:[41,42]



(XXXVII) (XXXVIII)

R=Me, Ph .

The reactions of the salts (XL) with hydrogen sulphide in a methanol–pyridine mixture proceed analogously with formation of compounds (XLI) and (XLII):[41,43]



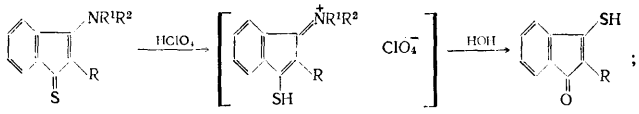
(XL) (XLI) (XLII)

## III. β-MERCAPTO- AND β-ALKYLTHIO-IMINIUM SALTS

### 1. β-Mercaptoiminium Salts

Stable 3-mercaptoprop-2-eneiminium salts and their cyclic analogues are known. It has been shown by $^1$H NMR [44] that 3-(*NN*-dimethylamino)-2-phenyl-1-indenethione (XIV) is

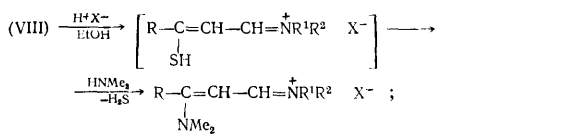
protonated by perchloric acid in acetone with formation of a solution of 3-mercapto-*NN*-dimethyl-2-phenylindene-1-iminium perchlorate (XLIII). The latter hydrolyses at the C=N bond and is converted into 3-mercapto-2-phenyl-1-indenone (XII):



(XIV) (XLIII) (XII), 80%

R=Ph; $R^1=R^2=Me$ .

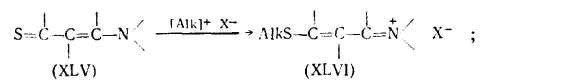
A mechanism has been proposed for the aminolysis of 3-aminoprop-2-enethione (VIII) in an acid medium at 20 °C, in which the intermediate formation of the 3-mercaptoprop-2-eneiminium salt (XLIV) is postulated:[11]



$R^1=R^2=Me$ .

## 2. β-Alkylthioiminium Salts

The salts (XLVI), containing the β-alkylthiopropeneiminium group, are obtained from the corresponding enaminothioketone (XLV) using the same alkylating agents as in the synthesis of their 3-alkoxy-analogues (see above). Methyl fluorosulphonate is used for this purpose:[45]

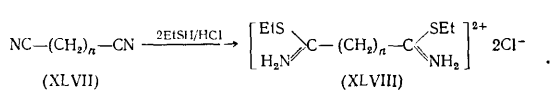


(XLV) (XLVI)

X=Hal, $BF_4$, $FSO_3$, $SO_4$ .

Stable salts of the propene,[46,47] indene[48] and cyclohexene[6] series and the thio- and dithio-esters of squaric[49] and dicarboxylic[43] acids have been synthesised in this way in high yields. Enaminothioketones are alkylated regiospecifically and more readily than enaminoketones.[21,48]

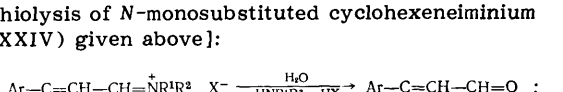
Dicarboxylic acid thioesters (XLVIII) are also obtained by the reaction of the corresponding dinitriles (LXVII) with ethanethiol and hydrogen chloride:[43,50]



(XLVII) (XLVIII)

*Hydrolysis.* The few studies which have been made on the hydrolysis of β-alkylthio-substituted αβ-unsaturated iminium salts nevertheless embrace compounds of various classes, which makes it possible to discover a general feature of the process—the direction of attack by the hydroxide ion on the C=N bond.

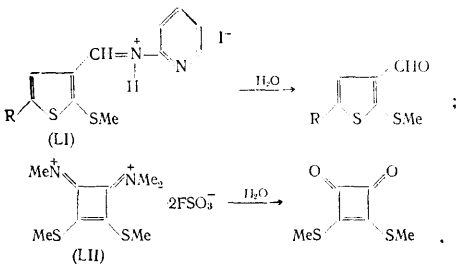
The hydrolysis of *NN*-disubstituted 3-methylthioprop-2-eneiminium salts (XLIX) leads to the corresponding β-alkylthioaldehydes (L).[46,47,51] The *N*-monoaryl-substituted iodides (XLIXb) are hydrolytically stable [cf. data on the hydrothiolysis of *N*-monosubstituted cyclohexeneiminium salts (XXIV) given above]:



(XLIX) (L)

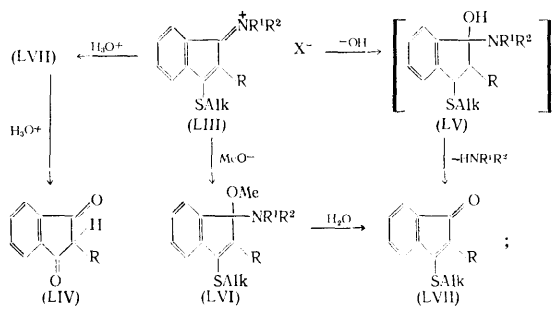
Ar=Ph, 4-$ClC_6H_4$, 4-$MeOC_6H_4$; $R^1R^2=(CH_2)_4$, $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$ (a); $R^1=H$, $R^2=Ar$ (b); X=I .

The salts of the thiophen series (LI)[52] as well as derivatives of squaric acid (LII) are hydrolysed analogously:[45]



(LI) (LII)

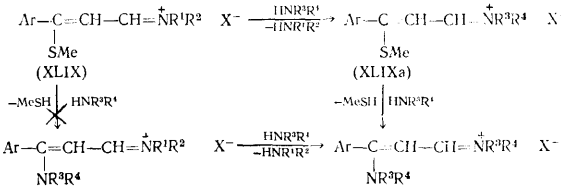
The hydrolysis of 3-alkylthio-2-phenylindene-1-*NN*-dimethyliminium salts (LIII) has been studied in greatest detail.[48] Alkaline hydrolysis in DMF leads to their ready conversion into 3-alkylthio-2-phenyl-1-indenones (LVII). The *gem*-alcohols (LV) are probably intermediates in this reaction, since the corresponding *gem*-methoxyamino-derivatives were isolated on methanolysis of the salt (LIII). Their hydrolysis leads to the alkylthioketones (LVII). The final product of the acid hydrolysis of the salt (LIII), which proceeds via the formation of the alkylthioketones (LVII), is 2-phenyl-1,3-indandione (LIV):[48]



(LIV) (LVI) (LVII)

R = Ph; $R^1=R^2=Me$ .

*Aminolysis.* 3-Alkylthiopropeneiminium salts (XLIX) react with alkyl- and aryl-amines to form the salts of enaminoimines with identical substituents at different nitrogen atoms [compounds (LVIIIa)].[32,33] Of the two possible reactions (XLIX) → (LVIII) → (LVIIIa) and (XLIX) → (XLIXa) → (LVIIIa), the latter occurs.[32] The sequence of reaction stages (transamination–substitution) has been demonstrated by the reaction of compound (LVIIIa; Ar = 4-$MeOC_6H_4$; $R^3=R^4=Et$; X = $ClO_4$) with an excess of dimethylamine. It was found that the reaction of the resulting asymmetrically substituted salt [4-$MeOC_6H_4$–$C(NMe_2)$=CH–CH=$NEt_2$]$^+ClO_4^-$ dimethylamine, modelling the stage (LVIII) → (LVIIIa), does not take place:



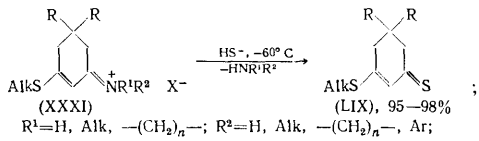
(XLIX) (XLIXa) (LVIII) (LVIIIa)

Ar=Ph, 4-$MeOC_6H_4$; $R^1=R^2=Alk$; $R^3=R^4=Alk$ или $R^3$ = H, $R^4$ = Ar; X = $ClO_4$, I .

When the salts (XLIX) are acted upon by arylamines in ethanol, the transamination products (XLIXa) are formed in 90% yield. The methylthio-group is exchanged for the amino-group [(XLIXa) → (LVIIIa)] only in acetic acid.[33] The perchlorates (XLIX; Ar = Ph or 4-$MeOC_6H_4$; X = $ClO_4$) form

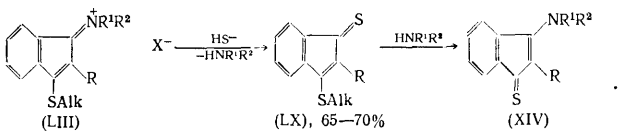
the corresponding enaminoimines (LVIIIa) in a high yield (up to 88%). On the other hand, the enaminoimine salts (LVIIIa) are obtained from the analogous iodides (XLIX) in a yield not exceeding 38%.

*Hydrothiolysis.* The study of the reactions of β-alkylthio-substituted αβ-unsaturated iminium salts with sulphur-containing nucleophiles was first undertaken in relation to cyclohexene derivatives.[6,21] 3-Alkylthiocyclohex-2-ene-1-iminium salts (XXXI) react with hydrogen sulphide in DMF in the presence of triethylamine at −60 °C via the C=N bond (see above), similarly to the 3-alkoxy-derivatives, forming 3-alkylthiocyclohex-2-ene-1-thiones (LIX). These compounds contain the little known structural fragment AlkS−C=C−C=S:

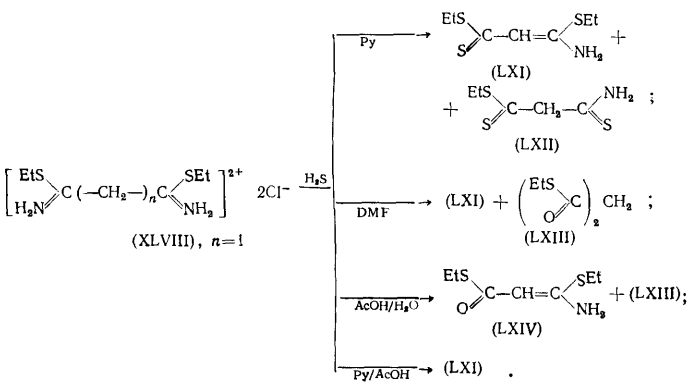



$R^1$=H, Alk, $-(CH_2)_n-$; $R^2$=H, Alk, $-(CH_2)_n-$, Ar; X=$BF_4$, I .

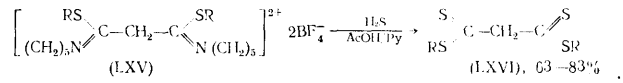
3-Alkylthio-2-arylindene-1-iminium salts (LIII) react with hydrogen sulphide in methanol at 20 °C to form 3-alkylthio-2-arylindene-1-thiones (LX). When the salt (LIII) is treated with sodium hydrogen sulphide, the corresponding enaminothioketones (XIV) are formed rapidly in accordance with the scheme (LIII) → (LX) → (XIV):[48]



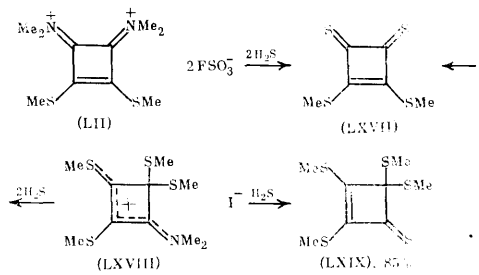

The hydrothiolysis of the dihydrochloride of *SS*-diethylpropanedithiodiimidic acid (XLVIII) has been investigated in detail.[50] This salt does not interact with liquid hydrogen sulphide at −78 °C, while at 20 °C in pyridine, DMF, DMSO, or acetic acid, several compounds (LXI)–(LXIV) are formed in yields ranging from 20 to 40%, which indicates the non-regiospecificity of the hydrothiolysis. The formation of the carbonyl compounds (LXIII) and (LXIV) has been explained[50] by the hydrolysis of the initial dihydrochloride (XLVIII) as a result of the treatment of the reaction mixture with an aqueous solution of sodium bicarbonate:




*N*-Unsubstituted salts (XLVIII) react with hydrogen sulphide in a pyridine–acetic acid mixture, retaining one amino-group, while their piperidine analogues (LXV) lose both amino-groups under these conditions and give rise to the ester of the bisdithiocarboxylic acid (LXVI):[41]

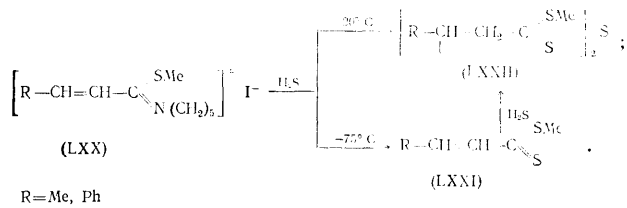



The hydrothiolysis of both dimethylamino-groups in methylthiocyclobut-2-ene-1,4-bis-*NN*-dimethyliminium bisfluorosulphonate (LII) proceeds readily. The product of this reaction is 2,3-bis(methylthio)cyclobut-2-ene-1,4-dithione (LXVII), whose chemical properties have been vigorously investigated:[49,53]




The hydrothiolysis of 2,3,4,4-tetrakis(methylthio)cyclobut-2-ene-1-*NN*-dimethyliminium iodide (LXVIII) either proceeds immediately via two pathways to the dithiodiketone (LXVII) or the reaction involves only the iminium group, which leads to the monothioketone (LXIX).[53]

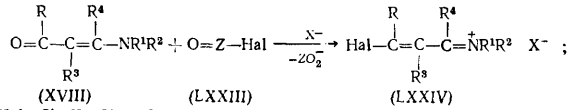
1-Methylthioprop-2-ene-1-piperidinium iodide (LXX), which is a structural isomer of the 3-alkylthioprop-2-ene-1-iminium salts (XLIX), reacts with hydrogen sulphide in a tetrahydrofuran (THF)—pyridine mixture at −75 °C, forming methyl dithiocinnamate (LXXI).[42] The sulphide (LXXII) has been obtained at 20 °C by the reaction of compound (LXX) with hydrogen sulphide (cf. the reaction described in Section III, 2 above):




R=Me, Ph

## IV. β-HALOGENOIMINIUM SALTS

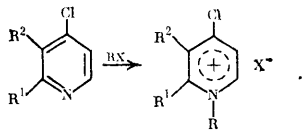
There exist two main synthetic approaches to the preparation of β-halogeno-substituted αβ-unsaturated iminium salts (LXXIV).[2] The first is based on the corresponding modification of the C(1)- and C(3)-structural elements in the initial compound with the propene group. The second involves the construction of the propene skeleton of the salt from suitable components containing the C(1)- and C(2)-, C(3)-fragments of the required compound. Halogenoiminium salts are obtained by the first method as a result of the interaction of β-aminovinylcarbonyl compounds (LXXX) with various chlorinating agents (LXXIII) ($POCl_3$, $COCl_2$, $SO_2Cl_2$, and ClCOCOCl) or even with $PCl_5$. Treatment with the analogous brominating agents leads to the corresponding bromo-substituted salts. Compounds (XVIII) and (LXXIII) vary structurally within relatively wide limits:[28]



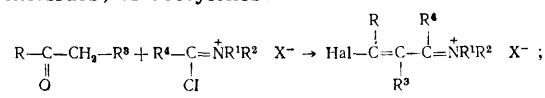
(XVIII) (LXXIII) (LXXIV)

Hal=Cl; X=Cl, $ClO_4$, $OPOCl_2$ .

The first method is also used to synthesise substituted pyridinium salts by alkylating 4-chloropyridines:[2]



In the synthesis of 3-chloroprop-2-eneiminium salts (LXXIV) via the formation of the C(1)–C(2) bond, one uses methyleneketones and the salts of imidoyl chlorides, mainly formimidoyl chloride, or even the phosgeneiminium salt, whose mobile chlorine atom is readily substituted by a nucleophile.[2] The initial methylenecarbonyl compound can be replaced, for example, by enamines, enol ethers, acetals, vinyl chlorides, or acetylenes:[2]

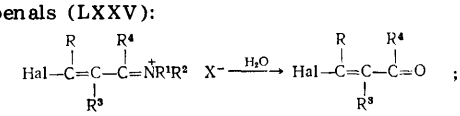


(LXXIV)

$R^4$=H, Cl; Hal=Cl .

The second method is of the greatest synthetic importance. However, the first method is so far the only one available in many instances, for example, for cyclic derivatives.

*Hydrolysis.* Little information is available about the hydrolysis of 3-halogenoprop-2-eneiminium salts and their cyclic analogues.[54–56] 3-Halogeno-prop-2-ene-1-*NN*-dimethyliminium salts (LXXIV) are hydrolysed with retention of the C–Hal bond, which leads to the formation of 3-halogenopropenals (LXXV):

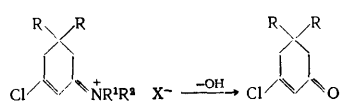


(LXXIV) (LXXV)

$R^4$=H; Hal=Br, Cl; X=Cl, $ClO_4$, $OPOCl_2$, *o*-$MeC_6H_4SO_2O$ .

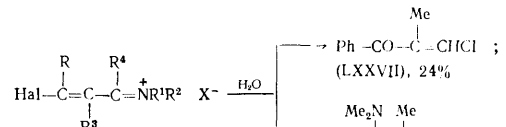
The nature of the substituents R and $R^3$ has a marked effect on the hydrolytic stability of the salts (LXXIV). The salts (LXXIV; $R^1$ = H or Me; $R^3$ = H), which have no substituents at the central carbon atom, are distinguished by an extremely high stability in aqueous solution, which can be accounted for[56] by the high degree of conjugation in the pentad fragment.

The salts (LXXIV) having substituents R with a large effective volume (R = Ph or t-Bu) and $R^3$ = H are readily hydrolysed on refluxing with an aqueous solution of sodium acetate. 3-Chlorocyclohex-2-ene-1-pyrrolidinium perchlorate (LXXVI) is also hydrolysed at the C=N̂ bond on heating in methanol to which a 10% NaOH solution has been added:[28]



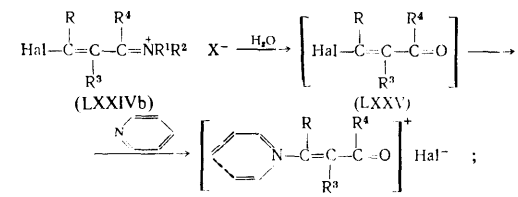
(LXXVI) 95%

3-Chloro-2-methyl-1-phenylprop-2-ene-1-*NN*-dimethyliminium chloride (LXXIVa) is hydrolysed via two pathways with formation of 3-chloro-2-methyl-1-phenylprop-2-en-1-one (LXXVII) and more than 50% of the aldehyde (LXXVIII). The low yield of the ketone (LXXVII) can be accounted for by steric hindrance, which prevents the hydrolysis of the C=N̂ bond:[54]



(LXXIVa), R=H, $R^1$=$R^2$=$R^3$=Me, $R^4$=Ph, Hal=X=Cl .

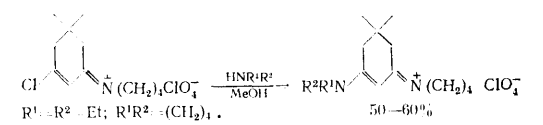
Treatment of the 3-chloro-3-(4-tolyl)prop-2-ene-1-iminium salt (LXXIVb) with pyridine in 90% ethanol yielded the chloride (LXXIX).[57] It may be that the first stage of this reaction is the hydrolysis of the salt (LXXIVb) at the C=N̂ bond and the formation of 3-chloropropenal (LXXV), whose aminolysis at the C–Cl bond leads to compound (LXXIX):



(LXXIVb) (LXXV) (LXXIX)

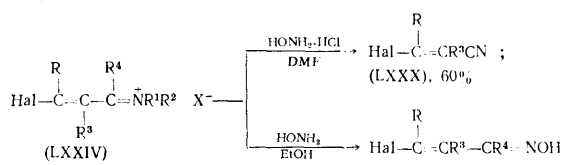
R=4-$MeC_6H_4$, $R^3$=$R^4$=H, Hal=Cl .

*Aminolysis.* β-Chloro-substituted αβ-unsaturated iminium salts react with amines, substituting the chlorine atom for the amino-group, which leads to salts of enaminoimines,[28,58] for example:



$R^1$=$R^2$=Et; $R^1R^2$=$(CH_2)_4$ . 50–60%

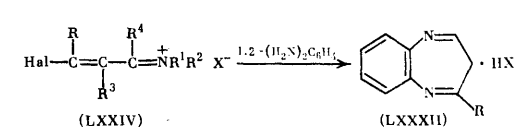
The ability of chloroiminium salts to react with nucleophiles via the C=N̂ bond has attracted much attention by investigators. Thus the reaction of arylpropene derivatives (LXXIV) with hydroxylamine hydrochloride in DMF has led to a simple way of synthesising the corresponding 3-chloropropenyl cyanides (LXXX).[59] Treatment of the salt (LXXIV) in ethanol with a hot aqueous solution of hydroxylamine leads to a high yield of 3-aryl-3-chloroprop-2-ene-1-aldoxime (LXXXI):[60]



(LXXIV) (LXXX), 60% (LXXXI), 92%

R=4-$MeC_6H_4$, 4-$MeOC_6H_4$; $R^3$=$R^4$=H; Hal=Cl .

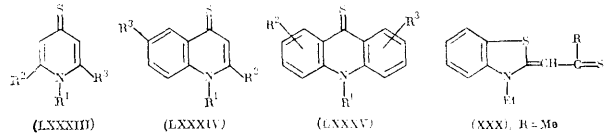
When the salts (LXXIV) react with 1,2-phenylenediamine, both electrophilic centres—the C(1) and C(3) atoms—are attacked by the nucleophile and 2-aryl-3*H*-1,5-benzodiazepinium salts (LXXXII) are formed:[61]



(LXXIV) (LXXXII)

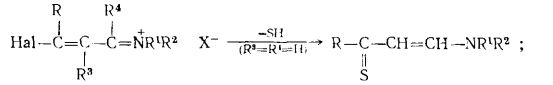
R=Ar, $R^3$=$R^4$=H, Hal=Cl .

*Hydrothiolysis.* The reactions of salts of nitrogen-containing heterocyclic bases incorporating the $Cl-\overset{|}{C}=C-\overset{|}{C}=\overset{+}{N}\diagup X^-$ group with sodium sulphide of hydrogen sulphide in alcohol has been used for a long time to synthesise the corresponding heterocyclic enaminothioketones. Sodium thiosulphate and *NN*-dimethyldithiocarbamate,[62] and thiourea[63] have also been used for the thiolysis of salts of this type. Substituted 4-thiopyridones (LXXXIII),[63,64] 4-thioquinolones (LXXXIV),[64,65] 9-thioacridones (LXXXV),[62,66,67] and 3-ethyl-2-thioacetonylidene-2,3-dihydro-1,3-benzothiazole (XXX)[68] have been obtained in this way in high yields:



(LXXXIII) (LXXXIV) (LXXXV) (XXX), R=Me

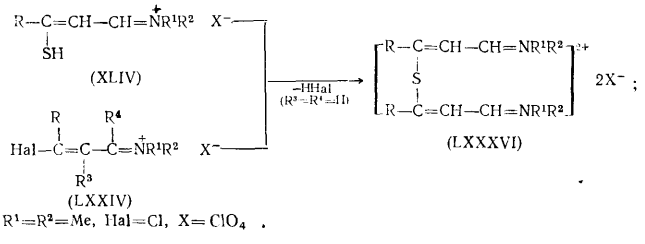
The synthesis of the aliphatic enaminothioketones (VIII) is based on the reactions of 3-aryl-3-chloroprop-2-ene-1-*NN*-dimethyliminium salts (LXXIV) with sodium sulphide in aqueous DMF solution or in a DMF–ethylene glycol mixture[69] and also with sodium thiosulphate in alcohols.[70] The temperature (20–60 °C) and the reaction time (2–24 h) are determined by the nature of the aryl substituent:



(LXXIV) (VIII), ~80%

R=Ph, 4-$MeC_6H_4$, 4-$BrC_6H_4$, 1-$C_{10}H_7$ etc.; $R^1=R^2=Me$; Hal=Cl .

When the reaction mixture is treated with a primary or secondary amine, amine exchange takes place and leads to the corresponding enaminothioketones $R-C(=S)-CH=CH-NR^1R^2$ (VIII) with a wide variety of nitrogen-containing substituents.[70] If the molar ratio of sodium thiosulphate and the salt (LXXIV) is 1:2, the reaction product is the sulphide compound (LXXXVI) (yield 80%). It is apparently obtained as the final result of the condensation of the initial 3-chloropropeneiminium salt (LXXIV) with the 3-mercaptopropeneiminium salt (XLIV) formed initially:

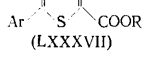


(XLIV) (LXXXVI)

(LXXIV)

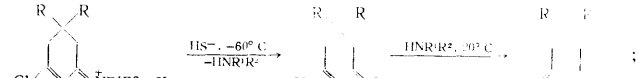
$R^1=R^2=Me$, Hal=Cl, X=$ClO_4$ .

The salts (LXXIV) react with mercaptoacetate esters $HSCH_2COOR$ in the presence of sodium methoxide with elimination of the chlorine atom and the amino-group and the formation of cyclisation products—5-substituted thiophencarboxylates (LXXXVII):[71]



(LXXXVII)

Thus, until recently, the usual pathway in the reaction of compounds containing the $Cl-\overset{|}{C}=\overset{|}{C}-\overset{+}{C}=N\diagup$ group with sulphur-containing nucleophiles was believed to involve the substitution of the chlorine atom. However, it was established in 1979[2] that this reaction can proceed with dissociation of the C=N bond. Thus the interaction of 3-chlorocyclohex-2-ene-1-iminium salts (LXXVI) with hydrogen sulphide in DMF at −60 °C in the presence of triethylamine leads to 3-chlorocyclohex-2-ene-1-thione (LXXXVIII). A compound containing the $Cl-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=S$ group was obtained in this way for the first time. The chlorothione (LXXXVIII) is a stable intermediate in the hydrothiolysis of the salt (LXXVI), since it interacts instantaneously with amines at 20 °C, forming the enaminothioketones (XXXII):[6,22]

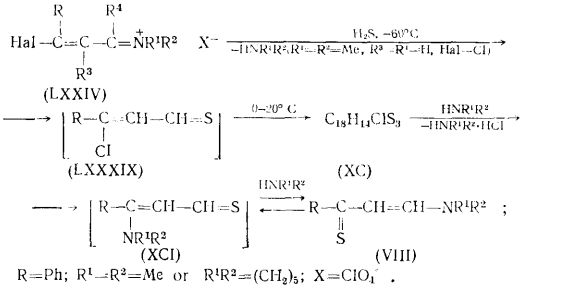


(LXXVI) (LXXXVIII), 87% (XXXII)

$R^1$=H, Alk, $-(CH_2)_n$; $R^2$=H, Alk, $-(CH_2)_n$, Ar; X=$ClO_4$ .

In addition it has been established[6] that the reaction of 3-chloro-3-phenylprop-2-ene-1-*NN*-dimethyliminium perchlorate (LXXIV) with hydrogen sulphide in DMF at −60 °C entails in the first place the elimination of dimethylamine, and not hydrogen chloride, and compound (XC) having the composition $C_{18}H_{14}ClS_3$ is produced. In this case the hydrothiolysis of the iminium group should have led to 3-chloro-3-phenylprop-2-ene-1-thial (LXXXIX), but the latter could not be isolated in a pure state. The absence of resolved signals in the IR, $^{13}C$ NMR, and $^1H$ NMR spectra of the product (XC) indicated its polymeric structure.

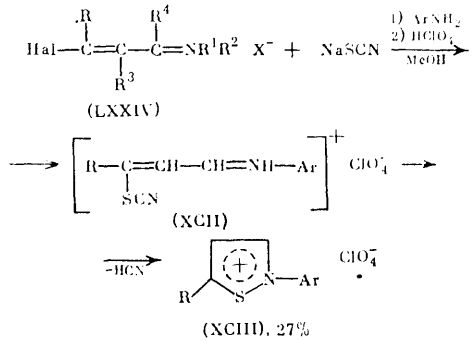
The hydrothiolysis product (XC) reacts rapidly with dimethylamine and piperidine at 20 °C.[6] The amine hydrochlorides isolated under these conditions indicate the involvement of the C–Cl bond in the reaction. However, the aminolysis products were not 3-(*NN*-dimethylamino)-(piperidino)-3-phenylprop-2-ene-1-thials (XCI) or the isomeric enaminothioketones (VIII), identical with those described previously.[70] Like their oxygen analogues,[55,72] the thials (XCI) formed initially probably isomerise in the presence of amines, which is the reason for the final outcome of the aminolysis of the product (XC):



(LXXIV) (LXXXIX) (XC) (XCI) (VIII)

R=Ph; $R^1=R^2=Me$ or $R^1R^2=(CH_2)_5$; X=$ClO_4$ .

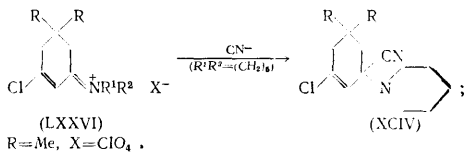
*Reaction with alkali metal thiocyanates.* The successive interaction of 3-chloroprop-2-ene-1-iminium salts (LXXIV) with thiocyanic acid and primary aromatic amines leads to 1,2-thiazolium salts (XCIII).[2] The authors[2] suggest that the reaction proceeds via the intermediate formation of 3-thiocyanatoprop-2-ene-1-iminium salts (XCII):



(LXXIV) (XCII) (XCIII), 27%

The reactions of the salts $ClCR{=}CH{-}CH{=}\overset{+}{N}R^1R^2\ X^-$ with KSCN (or NaSCN) in acetonitrile or DMF in the presence of catalytic amounts of tetra-alkylammonium iodide or crown-ether lead to 3-thiocyanato-substituted salts $NCSCR{=}CH{-}CH{=}\overset{+}{N}R^1R^2\ X^-$, where R = Ph, Ar, naphthyl, anthryl, heteroaryl, or PhCH = CH, $R^1$, $R^2$ = Alk, Ar or $R^1R^2 = (CH_2)_4$ or $(CH_2)_2O(CH_2)_2$, and X = Cl, $ClO_4$, or $PO_2Cl_2$, in 44–97% yield.[73]

*Cyanolysis.* The product of the reaction of 3-chloro-5,5-dimethylcyclohex-2-ene-1-piperidinium (LXXVI) with potassium cyanide in DMF is 3-chloro-1-cyano-5,5-dimethyl-1-piperidinocyclohex-2-ene (XCIV):[6]

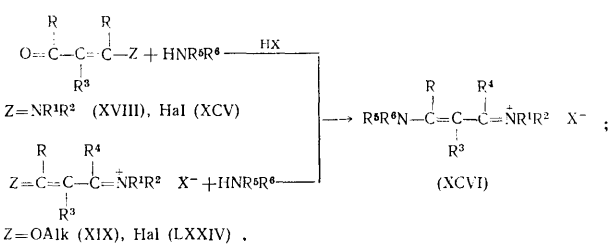


(LXXVI)
R=Me, X=$ClO_4$ .

The formation of the geminal aminonitrile (XCIV) shows that, in the first stage of the overall nucleophilic substitution reaction involving salts of type (LXXVI), the "soft" nucleophile adds to the C(1)=$\overset{+}{N}$ bond and not to the C(2)=C(3) bond.

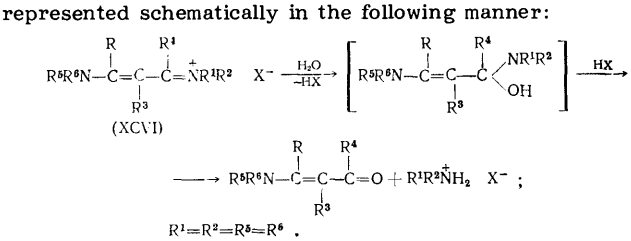
## V. β-AMINOIMINIUM SALTS

The reactions of compounds (XVIII) containing the β-aminovinylketone group or compound (XCV) containing the β-halogenovinylketone groups as well as the reactions of β-heterofunctional αβ-unsaturated iminium salts (XIX) and (LXXIV) with various amines are usually employed for the synthesis of enaminoimine salts (XCVI):[1]



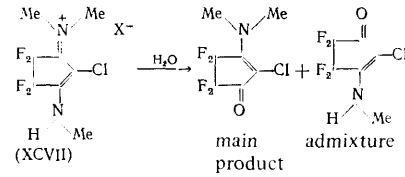
Z=OAlk (XIX), Hal (LXXIV) .

*Hydrolysis.* The hydrolysis of the enaminoimine salts (XCVI) substituted symmetrically at the nitrogen atoms can be represented schematically in the following manner:



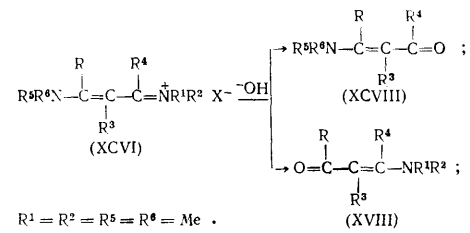
Depending on the structure of the salts, this reaction takes place in acid, neutral, or basic media.[1] The *N*-aryl-substituted salts of the indene enaminoimines are more resistant to hydrolysis than those unsubstituted at the nitrogen atom.[74]

In the case of asymmetrically substituted enaminoimine salts, the question arises of the carbon atoms to which the attack by the nucleophile is directed. The influence of steric factors on the outcome of the hydrolysis has been stressed in a study[75] of the hydrolysis of the 2-chloro-4,4,5,5-tetrafluoro-3-(*N*-methylamino)cyclopent-2-ene-1-*NN*-dimethyliminium salt (XCVII) and also in a review:[1]



(XCVII) main product admixture

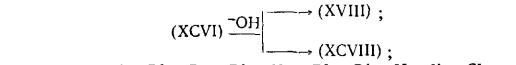
The mode of hydrolysis of tetrasubstituted aminopropeneimine salts (XCVI) is treated from the same standpoints:[1]



$R^1 = R^2 = R^5 = R^6 = Me$ .

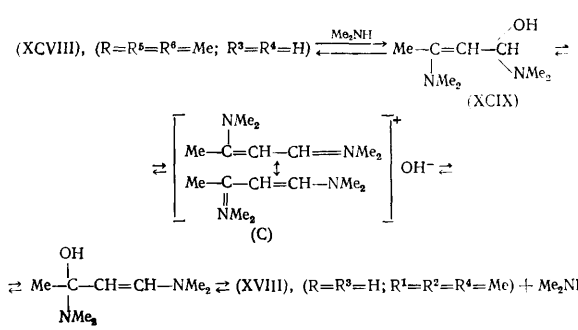
When R = Me or Ph and $R^4$ = H, mainly the enaminoaldehyde (XCVIII) is formed, while the isomer (XVIII) is a side product.

In another study[76] the mechanism of the reactions was treated in a different way. Two isomers, namely 4-(*NN*-dimethylamino)but-3-en-2-one (XVIII) and 3-(*NN*-dimethylamino)but-2-en-1-al (XCVIII), were isolated on hydrolysis of 3-methyl-3-(*NN*-dimethylamino)prop-2-ene-1-*NN*-dimethyliminium chloride (XCVI) with aqueous alkali:



R = $R^1 = R^2 = R^5 = R^6$ = Me; $R^3 = R^4$ = H; X = Cl .

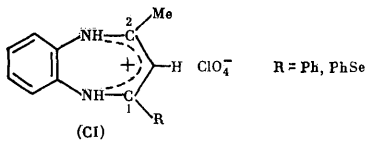
The hydrolysis of the salt (XCVI) at 25 °C and a reduced pressure leads to the aldehyde (XCVIII) in 55% yield. The authors[76] explained the formation of the two isomers (XVIII) and (XCVIII) on hydrolysis of the salt (XCVI) by the ability of the aldehyde (XCVIII) to isomerise readily to the ketone (XVIII) on treatment with dimethylamine. It was suggested that the *gem*-hydroxyamine (XCIX), formed as a result of the addition of dimethylamine to the aldehyde (XCVIII), is in equilibrium with the dissociated form (C). Its mesomeric cation is converted into the aldehyde (XCVIII) or the ketone (XVIII) after recombination with a hydroxide ion and the elimination of dimethylamine:



(XCIX)

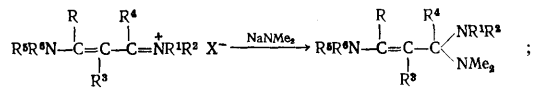
(C)

the hydroxide ion attacks the sterically most shielded C(1) atom:



(CI) R = Ph, PhSe

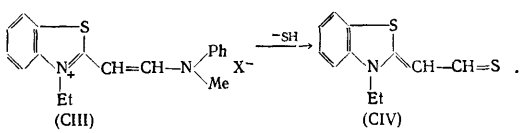
*Aminolysis.* The aminolysis of enaminoimine salts is usually terminated by transamination and has little preparative value.[78] The reaction probably proceeds via the formation of a *gem*-diamine. When 3-(*NN*-dimethylamino)prop-2-ene-1-*NN*-dimethyliminium salts (XCVI) were allowed to react with sodium NN-dimethylamide in benzene, the stable aminal (CII) was obtained:[79]



(XCVI) (CII), 62%

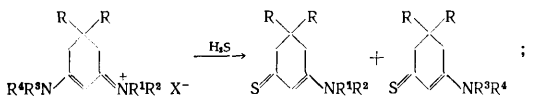
$R = R^3 = R^4 = H$; $R^1 = R^2 = R^5 = R^6 = Me$; $X = ClO_4$, $MeSO_4$ .

*Hydrothiolysis.* The hydrothiolysis of enaminoimines was first described in relation to the reaction of a 3-ethyl-2-[2-(*N*-methyl-*N*-phenylamino)vinyl]benzothiazolium salt (CIII) with sodium hydrogen sulphide in methanol, which led to a satisfactory yield of the enaminothial (CIV):[29]



(CIII) (CIV)

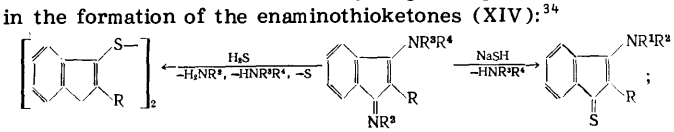
The hydrothiolysis of 3-piperidinocyclohex-2-ene-1-iminium salts (XXIX) does not proceed unambiguously. Their C(1) and C(3) atoms have similar reactivity indices,[23] which is apparently the cause of the simultaneous formation of the two enaminothioketones (XXXII) and (XXXIIa):



(XXIX) (XXXII) (XXXII a)

$R^1R^2 = (CH_2)_5$; $R^3 = H$; $R^4 = CH_2Ph$, Ph, 4-$MeOC_6H_4$ .

The reactions of 3-amino-2-phenylindene-1-imines (CV) with hydrogen sulphide in the presence of piperidine lead to a reduction product—bis(indenyl)disulphide (XXXV), while the reactions with sodium hydrogen sulphide result in the formation of the enaminothioketones (XIV):[34]



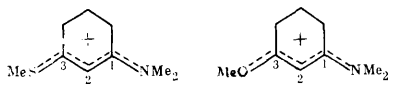
(XXXV) (CV) (XIV)

R = Ph, $R^1 = H$ .

## VI. QUANTUM-CHEMICAL ANALYSIS OF NUCLEOPHILIC SUBSTITUTION IN 3-ALKOXY- AND 3-ALKYLTHIO-CYCLOHEX-2-ENE-1-IMINIUM SALTS

Calculations have been carried out for the 3-methylthio- (A) and 3-methoxycyclohex-2-ene-1-*NN*-dimethyliminium (B) cations by the CNDO/2 method using a novel parametrisation.[6] The results of the calculation, which are presented solely for the chemically reactive $X-C=C-C=\overset{+}{N}Me_2$ fragment, are indicated in the molecular diagrams (A) and (B) (see Table) [the initial location of the positive charge on the N atom in the cations (A) and (B) is energetically more favourable to the extent of ~2 eV than its location on the O or S atoms]. Analysis of the molecular diagrams showed that both "soft" and "hard" nucleophiles attack the $C=\overset{+}{N}$ bond preferentially in the 3-methylthio-substituted cation (A)—this reaction pathway is subject to orbital and charge control.

Results of the calculations for the 3-methylthio- (A) and 3-methoxy-cyclohex-2-ene-1-*NN*-dimethyliminium (B) cations.



(A) (B)

| Atom or bond | Form (A) | | | Form (B) | | |
|---|---|---|---|---|---|---|
| | $q_i$, e | $k_i$ | $w$ | $q_i$, e | $k_i$ | $w$ |
| N | −0.063 | — | — | −0.071 | — | — |
| C(1) | 0.275 | 0.36 | — | 0.280 | 0.42 | — |
| C(2) | −0.104 | — | — | −0.191 | — | — |
| C(3) | 0.211 | 0.26 | — | 0.312 | 0.25 | — |
| S | 0.021 | — | — | — | — | — |
| O | — | — | — | −0.182 | — | — |
| $C(1)=\overset{+}{N}$ | — | — | 1.560 | — | — | 1.518 |
| C(1)=C(2) | — | — | 1.420 | — | — | 1.452 |
| C(2)=C(3) | — | — | 1.642 | — | — | 1.588 |
| C(3)—S | — | — | 1.071 | — | — | — |
| C(3)—O | — | — | — | — | — | 1.147 |

Notation: $q_i$ are the atomic charges, $k_i$ are the relative contributions of the atomic $\pi$ orbitals of the lowest unoccupied molecular orbital, and $w$ are the Wiberg bond indices.

In the case of the 3-methoxy-substituted cation (B), "soft" nucleophiles should react preferentially via the $C=\overset{+}{N}$ bond (orbital control predominates), while "hard" nucleophiles should react via the C—O bond (charge control predominates), which can be accounted for by the greater electronegativity of the MeO group compared with MeS.

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Thus the problem of the analysis of the reactions considered here is fairly complex, since the aim of the majority of the published studies (which have been very numerous—cf. Hünig[80]) was not a specific investigation of the reactions of unsaturated iminium salts with nucleophiles under comparable conditions. Instances of the hydrolysis, aminolysis, and hydrothiolysis of such salts at the C(1) atom as well as the C(3) atom or at both electrophilic centres are known. It is sometimes difficult to arrive at a correct conclusion about the course of the process owing to the hydrolysis of the final product and the occurrence of other side reactions. However, the practical usefulness of further more extensive investigation of nucleophilic substitution in iminium salts has been demonstrated by recent studies,[6,81] which indicated ways of synthesising new thio-derivatives of cyclohexene and indene on the basis of these reactions.

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# Reactions of Organic Compounds with Dissociation of N-N Bonds

M.F.Marshalkin and L.N.Yakhontov

Reactions involving the dissociation of single N-N bonds which have been carried out during the last decade and which are important for organic chemistry are surveyed. New data on the reductive cleavage of such bonds, various rearrangements, N-N bond dissociation reactions with simultaneous *N*-alkylation, and thermal, electrochemical, and photochemical processes are examined. Attention is concentrated on fundamentally new reactions, on studies of the reaction mechanisms, and on the development of methods extending the preparative scope of organic synthesis.
The bibliography includes 118 references.

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## I. INTRODUCTION

Reactions proceeding with dissociation of N–N bonds in both cyclic and acyclic compounds occupy a major place in organic chemistry. Owing to the repulsion between the *p* orbitals of neighbouring nitrogen atoms, the length of a single N–N bond (1.40 nm) exceeds the sum of the radii of the two nitrogen atoms ($0.53 \times 2 = 1.06$ nm). A characteristic feature of this bond is its very low dissociation energy (37 kcal $mol^{-1}$) compared with other single bonds most frequently encountered in organic compounds (for example, the energy is 80 kcal $mol^{-1}$ for the C–C bond, 66 kcal $mol^{-1}$ for the C–N bond, and 64 kcal $mol^{-1}$ for the S–S bond).

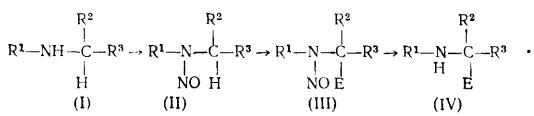
The above features of the N–N bond are responsible, under conditions where there is a possibility of competing reactions, for its preferential dissociation compared with the dissociation of the C–C or C–N bonds. This entails the formation of either the corresponding amino-derivative, or unstable products with an electron sextet at the nitrogen atom of the type of nitrenes, which are stabilised by further addition reactions, rearrangements, etc., or unstable free radicals, which recombine or undergo other radical processes ensuring the stabilisation of the molecule, are generated.

In our earlier review[1] an attempt was made for the first time to give a systematic account of the extensive literature data on the methods for the dissociation of single N–N bonds in organic compounds. The present review describes the advances during the last decade in the studies on organic compounds involving the dissociation of N–N bonds. Attention is concentrated on the examination of fundamentally new reactions, new studies on reaction mechanisms, and on the search for fundamentally new ways of employing processes of this type in preparative organic chemistry rather than on numerous new applications of compounds described previously.

## II. REDUCTIVE CLEAVAGE OF N–N BONDS

The hydrogenolysis of N–N bonds is one of the commonest methods for the conversion of various azines, azides, hydrazines, and their derivatives into the corresponding amines. The methods for the reductive cleavage of N–N bonds published up to 1972 have been examined in detail in the authors' previous review[1] as well as other reviews.[2-6]

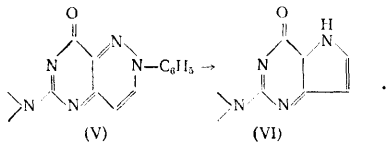
A new general method for the introduction of various substituents at the C(1) atom in secondary amines (I), based on their nitrosation, treatment of the nitroso-derivatives (II) with powerful bases and electrophiles, and reductive cleavage of the N–N bond in the nitrosoamine (III) in order to remove the nitroso-group, has been developed during the last decade:[7]



The last stage of the synthesis of compound (IV) is effected on the basis of a specially developed method for the reductive denitrosation of compound (III) with hydrogen in the presence of small amounts of Raney nickel.[8] This method proved to be suitable for compounds which are unstable in acid media, the other functional groups present in the substance (apart from the readily reducible olefinic and β-keto-groups), being unaffected under these conditions, which is the reason for its significant advantages over the earlier method for the denitrosation of amines with cleavage of the N–N bond in acid media.[9]

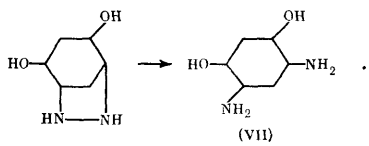
A method for the hydrogenolysis of the N–N bond in hydrazobenzene with formation of aniline via hydrogen transfer from 2-propanol to hydrazobenzene, catalysed by the triphenylphosphine complexes of rhodium and ruthenium, was published during the same period.[10]

By analogy with the other methods for the reductive cleavage of the N–N bond in pyridazine compounds indicated in the earlier review,[1] which lead to ring contraction, new syntheses have been developed for 5*H*-pyrrolo[3,2-*g*]-pyrimidines (V).[11] They include a stage involving the reduction of pyrimido[5,4-*c*]pyridazines (V) in the presence of a nickel or palladium catalyst.[11] The reductive opening of the pyridazine ring with dissociation of the N–N bond and the subsequent closure of a five-membered ring, the 4,6-diazaindole system (VI), are then observed:



(V) (VI)

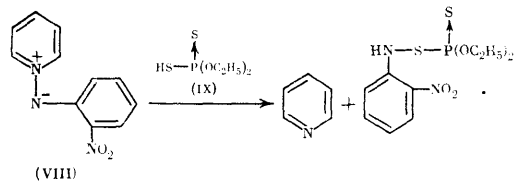
The catalytic reductive cleavage of both exocyclic[12] and endocyclic[13] N–N bonds in the synthesis of aminocyclitols (VII) has acquired considerable importance:



(VII)

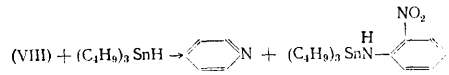
In view of the increasing importance of the problem of the protection of the environment, a study[14] in which a general method was proposed whereby various hydrazine compounds, including substances with a carcinogenic activity, can be made harmless by the reductive cleavage of their N–N bond with conversion into the corresponding less dangerous amino-derivatives, has attracted special attention.

Reduction with dissociation of this bond by a nucleophile, namely diethyl phosphinodithioic acid (IX), has been described for a compound with a semipolar N–N bond of the N-iminopyridinium type, namely the betaine (VIII):[15]

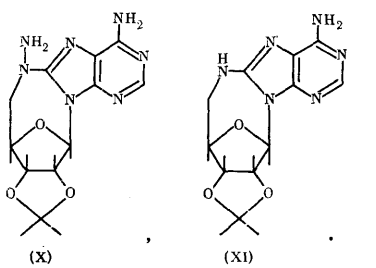


(VIII)

The same type of reaction takes place on treatment of compound (VIII) with tributyltin hydride[16] in the presence of αα′-azobisisobutyronitrile and is believed to be of the radical type:



In contrast to the reactions involving the reductive cleavage of N–N bonds described above, the oxidative cleavage of such bonds is also known and can be illustrated in relation to the deamination of the *N*-amino-derivatives (X) to give compound (XI) by oxidants such as iodine pentoxide, lead tetra-acetate, potassium permanganate, and sodium metaperiodate:[17]



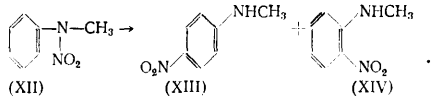
(X) (XI)

The deamination of 1,1-disubstituted aromatic hydrazines with the aid of nitrous acid, which apparently proceeds via *N*-diazonium salts, has also been studied in detail in recent years.[18]

## III. REARRANGEMENTS INVOLVING THE DISSOCIATION OF N–N BONDS

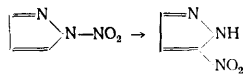
In addition to the sextet rearrangements of the type of the Curtius and Schmidt reactions and nitrile and various aryl-hydrazone rearrangements described in a previous review, publications dealing with new types of reactions, involving the cleavage of the N–N bond, have appeared during the last decade. At the same time, some of the reactions known previously not only came to be used more widely on a preparative scale but also have been the subject of more detailed theoretical and applied research.

For the acid-catalysed nitroamine rearrangement involving *N*-methyl-*N*-nitroaniline (XII), processes occurring in the presence of hydroquinone, which rules out an intermolecular reaction mechanism, were investigated, and it was shown that the yield of the *p*-nitro-isomer (XIII) relative to the *o*-nitro-amino-compound (XIV) increases appreciably with increase of the viscosity of the solution. According to the authors, this indicates the involvement of solvent molecules in the nitro-group migration processes:[19]



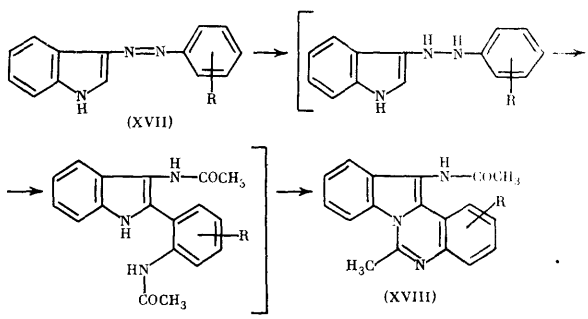
(XII) (XIII) (XIV)

The dissociation of the N–N bond accompanied by the rearrangement of the nitroamine type on thermolysis of 1-nitropyrazole (XV) to give 5-nitropyrazole (XV) and in other analogous reactions has also been described:[20]



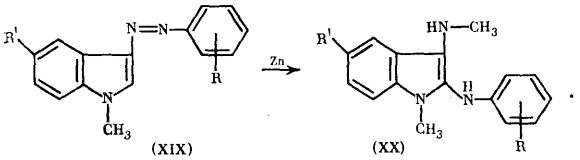
(XV) (XVI)

Vigorous studies on the mechanism of the benzidine rearrangement have continued.[21–27] When 3-arylozoindoles (XVII) were reduced with zinc in acetic acid in the presence of acetic anhydride and sodium acetate, a rearrangement of the *o*-benzidine type, proceeding with dissociation of the N–N bond and the formation, as a result of subsequent *N*-acylation and cyclisation, of derivatives of indolo[1,2-*c*]-quinazoline (XVIII) was observed:



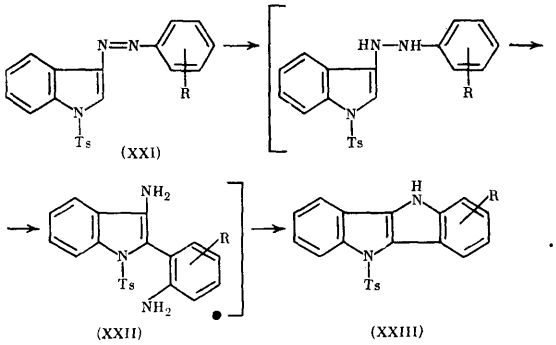
(XVII) (XVIII)

An analogous reaction occurs also for azo-compounds acylated at the pyrrole nitrogen atom[29] and also *N*-acetylin-doxyl arylhydrazones.[30,31] However, in the azo-compounds (XIX), which have a methyl substituent at the indole nitrogen, the dissociation of the N–N bond is accompanied by a semidine rearrangement with formation of 3-acetamido-2-arylamino-1-methylindoles (XX):[31]



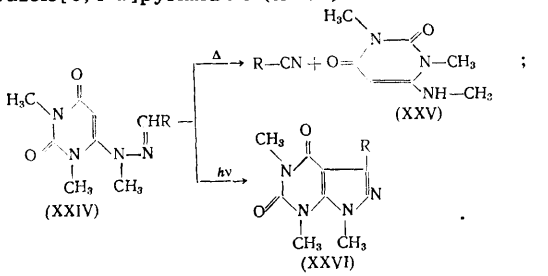
(XIX) (XX)

The reaction involving 3-aryl-1-tosylindoles (XXI) also proceeds with dissociation of the N–N bond accompanied by a rearrangement of the *o*-benzidine type, but the 3-amino-2-(*o*-aminoaryl)indoles (XXII) formed in this process cyclise with elimination of ammonia to give 5-tosylindolo[3,2-*b*]-indoles (XXIII):[32]



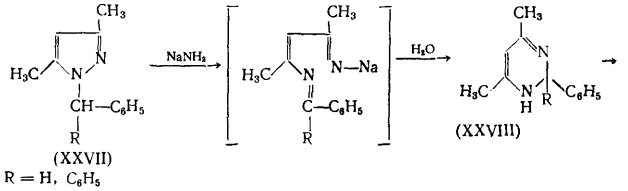
(XXI) (XXII) (XXIII)

Together with the nitrile rearrangement of hydrazones which has been widely investigated in previous studies,[1,33] the thermolysis of 1,3-dimethyl-6-(1-methylhydrazino)uracils (XXIV), which proceeds via a mechanism of the nitrile rearrangement type with dissociation of the N–N bond and the formation of 1,3-dimethyl-6-methylaminouracil (XXV), has been described in the last decade.[34,35] On the other hand, the photolysis of compound (XXIV) takes place without the cleavage of the N–N bond and leads solely to a derivative of pyrazolo[3,4-*d*]pyrimidine (XXVI):[36,37]



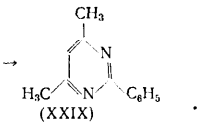
(XXIV) (XXV) (XXVI)

A new rearrangement has been discovered on heating to 155 °C α-benzyl-3,5-dimethylpyrazoles (XVII, R = H or $C_6H_5$) with sodium amide.[38] In this case the N–N bond of the pyrazole ring is broken with subsequent closure of the 1,2-dihydropyrimidine ring (XXVIII). If the reaction with compound (XXVII, R = H) is carried out at 185 °C, a further aromatisation of compound (XXVIII) is observed and the final product is 4,6-dimethyl-2-phenylpyrimidine (XXIX):



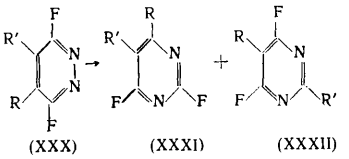
(XXVII) (XXVIII)

R = H, $C_6H_5$



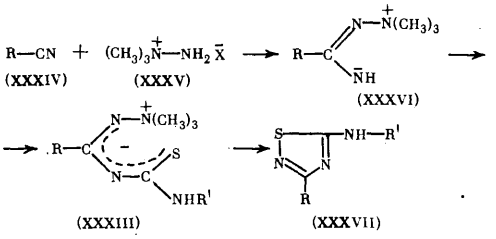
(XXIX)

An interesting thermal rearrangement has been observed for perfluoro-4,5-dialkylpyridazines or 4,5-diperfluoroalkylpyridazines, which are converted at 650 °C into perfluoro-4,5-dialkylpyrimidines (XXXI) and the corresponding diperfluoroalkyl derivatives while in the case of perfluoro-4,5-perfluoroethylpyridazines (XXX) a mixture of perfluoro-4,5-diperfluoroethylpyrimidines (XXXI) and perfluoro-2,5-diperfluoroalkylpyrimidines (XXXII) is obtained:[39,40]



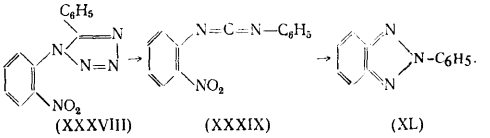
(XXX) (XXXI) (XXXII)

It has been found[41] that the thermolysis of the ylides derived from thiocarbamoylamidrazones (XXXIII) by the reaction of the nitriles (XXXIV) with trimethylhydrazinium chloride of the tosylate (XXXV) and potassium t-butoxide [42] followed by treatment of the ylides of unsubstituted amidrazones (XXXVI) thus produced with aryl or pentyl isocyanates leads to intramolecular nucleophilic attack by the sulphur atom on the N(2) atom with dissociation of the N–N bond, the elimination of triethylamine, and the formation of the corresponding 3-alkyl(aryl)-5-alkyl(aryl)amino-1,2,4-thiadiazoles (XXXVII) in high yields:



(XXXIV) (XXXV) (XXXVI) (XXXIII) (XXXVII)

The thermolysis of 1-(*o*-nitrophenyl)-5-phenyltetrazole (XXXVIII) involves the dissociation of the N–N bonds and the liberation of a nitrogen molecule with subsequent elimination of carbon dioxide from the resulting 1-(*o*-nitrophenyl)-3-phenylcarbodiimide (XXXIX) accompanied by the closure of the triazole ring. 2-Phenylbenzotriazole (XL) is formed in this reaction in yields up to 90%:[43]



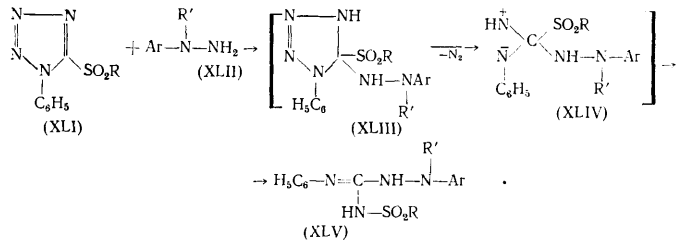
(XXXVIII) (XXXIX) (XL)

The formation of nitrogen and CO in this reaction was confirmed mass-spectrometrically. The corresponding 1-(*p*-nitrophenyl)-5-nitrotetrazole gives rise under these conditions to the thermally stable 1-(*p*-nitrophenyl)-3-phenylcarbodiimide as the main thermolysis product, which confirmed the reaction mechanism postulated by the author.

5-(*o*-Methoxyphenyl)-1-(*o*-nitrophenyl)- and (*oo'*-dimethoxyphenyl)-tetrazoles have been converted analogously in high yields into 2-(*o*-methoxyphenyl)- and 2-(*oo'*-dimethoxyphenyl)-benzotriazoles.[44]

Heating of 5-methanesulphonyl-1-phenyltetrazole (XLI) with arylhydrazines (XLII) above 170 °C leads to vigorous evolution of nitrogen as a result of the thermolysis of the

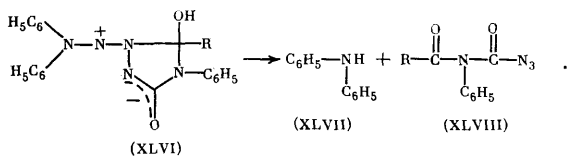
tetrazoline derivatives (XLIII) formed initially. Analogously to the process described previously,[45] the 1,3-dipoles (XLIV) apparently arise under these conditions and in the given instance are stabilised as a result of the migration, via the 2,3-shift mechanism, of the alkanesulphonyl groups from the carbon atom to the vicinal positively charged nitrogen atom with formation of 3-alkanesulphonyl-1-arylamino-2-phenylguanidine (XLV):[46]



(XLI) (XLII) (XLIII) (XLIV) (XLV)

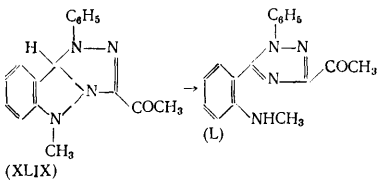
An analogous reaction takes place also when unsubstituted hydrazine is used instead of arylhydrazine.[47]

It has been shown that aminoazimines (XLVI) react at room temperature with bases such as ammonia, aliphatic amines, hydrazines, and aqueous alcoholic solutions of alkali metal hydroxides, being converted into the corresponding amines (XLVII) and azides (XLVIII) with dissociation of the N–N bond:[48]



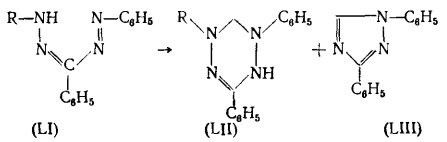
(XLVI) (XLVII) (XLVIII)

Under equally mild conditions, in tetrahydrofuran at room temperature but under the influence of catalytic amounts of concentrated hydrochloric acid, the N–N bond in 3-acetyl-5-methyl-1-phenyl-[1,9*b*]-dihydro-5*H*-1,2,4-triazolo[4,3-*b*]-indazole (XLIX) is broken with formation of 3-acetyl-5-(*o*-methylaminophenyl)-1-phenyl-1,2,4-triazole (L):[49]



(XLIX) (L)

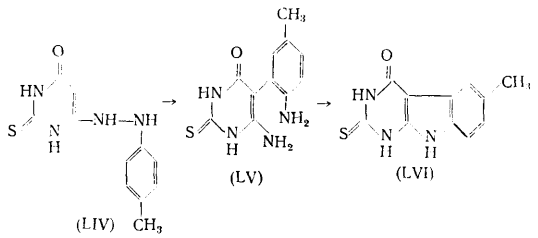
When 1-(2-methyl-5-tetrazolyl)-3,5-diphenylformazan (LI) was treated with formaldehyde, the cleavage of the N–N bond with formation of 1,3-diphenyl-1,2,4-triazole (LIII) was noted together with the closure of the tetrazine ring (LII):[50]



(LI) (LII) (LIII)

Despite its having been studied for a century, the widely known Fischer indole synthesis still continues to be one of the most investigated reactions in the chemistry of heterocyclic compounds. During the last decade alone, a series of new reviews[51–53] and chapters in monographs[6,54] were devoted to this reaction. The development of the concept of the [3,3]sigmatropic shift in the rearrangement stage with cleavage of the N–N bond,[52,56–58] the discovery of the "heterogeneous-catalytic Fischer reaction"[59–63] and its application to the synthesis of unsubstituted indole from acetaldehyde phenylhydrazone,[64] the discovery of the possibility of carrying out the Fischer reaction without acid catalysts ("thermal conversion into indoles",[65,66] conversion into indoles in the presence of bases[67–70] and under the conditions of "extractive base catalysis"[71]), and the discovery of the cationotropic rearrangement of arylhydrazides to 2-aminoindoles[72–77] and of the formation of γ- and δ-halogeno-carboxy-derivatives of indolylalkylamines on conversion of arylhydrazones into indoles[78] must be regarded as the most significant additional advances in the study of the Fischer reaction during this period.

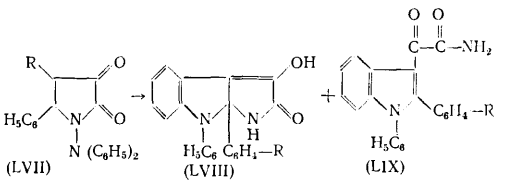
An acid-catalysed [3,3]sigmatropic rearrangement of the type of the Fischer reaction, proceeding with dissociation of the N–N bond, has been discovered for the reaction involving 6-(*p*-tolylhydrazino)-2-thiouracil (LIV). This led to the isolation of 5-(6-amino-3-tolyl)-6-amino-2-thiouracil (LV), which was converted on heating into the corresponding thio-derivative of 9*H*-pyrimido[4,5-*b*]indole-2,4-dione (LVI):[79]



(LIV) (LV) (LVI)

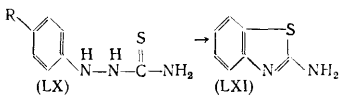
An analogous reaction had been described earlier also for 6-phenylhydrazinouracil.[80,81]

Certain other reactions involving the dissociation of the N–N bond and related to the Fischer indole synthesis have also been investigated. Thus the thermal cyclisation of 1-diphenylamino-2,3-dihydropyrrolidine-2,3-diones (LVII) yielded derivatives of pyrrolo[2,3-*b*]indole (LVIII) and (1,2-diphenyl-3-indolyl)glyoxylic amide (LIX):[82]



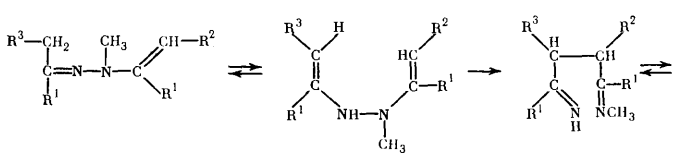
(LVII) (LVIII) (LIX)

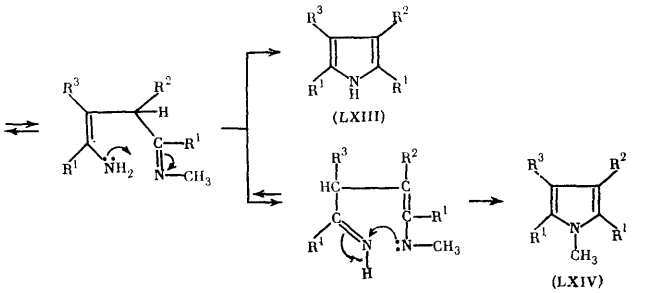
2-Aminobenzothiazoles (LXI) have been isolated in satisfactory yields after the Hugershoff reaction of 1-arylthiosemicarbazides (LX) with alkyl or halogeno-substituents in the benzene ring when these were treated with polyphosphoric acid:[83]



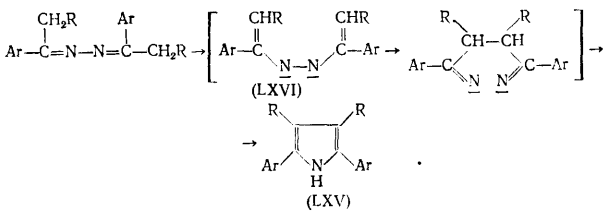
(LX) (LXI)

For the cyclisation of *N*-methylhydrazones of the enolisable ketones (LXII) to substituted pyrroles (LXIII) and (LXIV) under the conditions of the Piloty reaction, using titanium tetrachloride and molecular sieves as catalysts, a mechanism analogous to that of the corresponding reactions of azines has been proposed:[84,85]



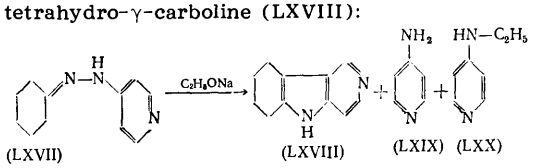



A mechanism involving the [3,3]sigmatropic rearrangement has been postulated as the most likely for a new synthesis of pyrroles (LXV) from the ketazine dianion (LXVI), which takes place in the presence of lithium diisopropylamide in tetrahydrofuran and not in an acid medium, in contrast to the Piloty reaction:[86]




## IV. REACTIONS INVOLVING THE DISSOCIATION OF THE N–N BOND WITH SIMULTANEOUS *N*-ALKYLATION

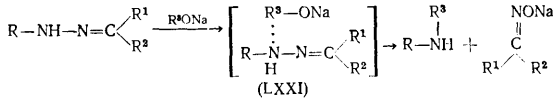
In the course of the study of the Fischer indole synthesis at the beginning of the 1970s, a new type of cleavage of the N–N bond with simultaneous *N*-alkylation was discovered.[87–89] It was found initially that, when cyclohexanone (4-pyridyl)-hydrazone (LVII) is heated with sodium ethoxide, the *N*-unsubstituted 4-aminopyridine (LXV) and 4-(*N*-mono-ethylamino)pyridine (LXX) are formed simultaneously with the occurrence of the normal Fischer reaction, which leads to the tetrahydro-γ-carboline (LXVIII):




It was shown thereby that the presence of acid catalysts is not an essential condition for the Fischer indole synthesis. Two reactions, which proceed under these conditions simultaneously with the indole synthesis, among which the first is associated with the thermal cleavage of the N–N bond in the hydrazone, apparently via a radical mechanism, and leads to the *N*-unsubstituted aminopyridine (LXIX), while the second has a mechanism apparently involving the intermediate formation of a four-membered cyclic transition state (LXXI), in which the synchronous cleavage of the C–O and N–N bonds is completed by the simultaneous formation of 4-(*N*-monoethylamino)pyridine and the sodio-derivative of cyclohexanone oxime, were observed.

The application of various pyridyl(aryl)hydrazones of aromatic aldehydes in this reaction makes it possible to rule out the possibility of indole synthesis and, by selecting the appropriate temperature, the process can be directed predominantly either towards *N*-unsubstituted or *N*-monoalkyl-substituted pyridyl(aryl)amines.

During the last decade, studies on the N–N bond cleavage reaction with simultaneous *N*-monoalkylation in the reactions of hydrazone and other analogous compounds with alkali metal alkoxides in accordance with the mechanism



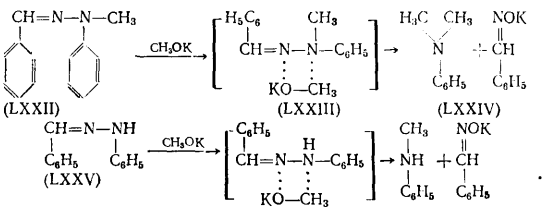

were developed further. The use in these reactions of the familiar[90] increase of the amount of ionic character in the oxygen–alkali metal bond in the sequence Li < Na < K < Rb < Cs made it possible to shift the process significantly, in the case of arylhydrazones. towards the formation of *N*-mono-alkylanilines and to achieve 80–90% yields of these compounds in reactions with potassium alkoxides. The analogous reactions with sodium alkoxides take place to an extent not greater than 10% and the main reaction pathway is the thermal decomposition of the arylhydrazones to *N*-unsubstituted anilines.[91,92]

The same influence on the main reaction pathway on passing from sodium to potassium and rubidium alkoxides has also been observed in the synthesis of *N*-monoalkylamino-derivatives of pyrazine, pyridazine, and pyrimidine from the corresponding benzaldehyde diazinylhydrazones and alkali metal alkoxides.[93]

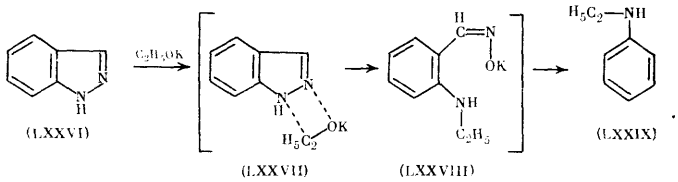
The isolation of 3-aminopyridazine, dibenzylamine, dibenzyl, benzyl alcohol, benzylidene-ethylamine and the products of the reaction of benzaldehyde (3-pyridazinyl)-hydrazone with sodium ethoxide at high temperatures indicates the radical character of the thermal decomposition of the hydrazones. As in other cases, the contribution of this reaction pathway increases with increase of temperature (the yields of the *N*-unsubstituted aminodiazines increase and those of *N*-monoalkylamino-derivatives diminish simultaneously).[93,94]

At the same time special experiments have shown that *N*-unsubstituted heteroaryl(aryl)amines cannot serve as intermediates in the formation of *N*-monoalkylheteroaryl-(aryl)amines, because they do not undergo *N*-alkylation when heated with alkali metal alkoxides at various temperatures.[94]

It is of interest that, when benzaldehyde *N*-methyl-*N*-phenylhydrazone (LXXII) was used as the initial compound in the reaction with potassium methoxide, the formation of a four-membered cyclic transition state (LXXIII) was nevertheless found to be possible despite a definite steric hindrance and the corresponding *NN*-dimethylaniline was obtained in a yield exceeding 20%. The formation of this compound even in trace amounts could not be detected by GLC in the reaction of benzaldehyde phenylhydrazone (LXXV) with potassium methoxide:[94]

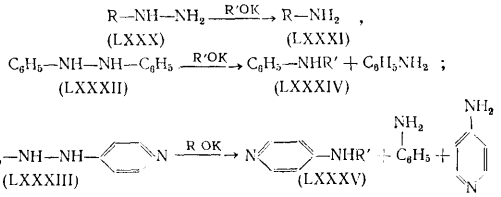



Indazole (LXXVI), which can be regarded as an endocyclic hydrazone, apparently undergoes similar reactions, on heating with potassium ethoxide, via the four-membered (in this instance tricyclic) transition state (LXXVII), in which synchronous dissociation of the C–O and N–N bonds take place. However, the resulting potassium salt of *o*-ethyl-aminobenzaldehyde oxime (LXXVIII) fragments with elimination of potassium cyanate or its elements and gives rise to a fairly high yield (60%) of *N*-monoethylaniline (LXXIX):[95]

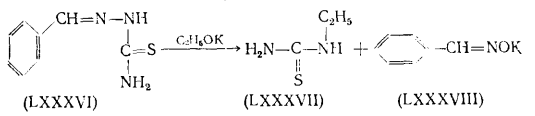


(LXXVI) (LXXVII) (LXXVIII) (LXXIX)

In contrast to *N*-monosubstituted hydrazines, which are cleaved at high temperatures by alkali metal alkoxides to give virtually quantitative yields of the primary amines (LXXXI), only[96] *NN'*-disubstituted hydrazines such as hydrazobenzene (LXXXII) and *N*-phenyl-*N'*-(4-pyridyl)-hydrazine (LXXXIII) give rise under analogous conditions to the corresponding *N*-alkylated amines (LXXXIV) and (LXXXV). The pathway involving the dissociation of the N–N bond with simultaneous alkylation is determined by the electron-accepting character of the residues at the hydrazine nitrogen atoms, which influence the polarity and polarisability of the N–N bond. For example, in the reaction of *N*-phenyl-*N'*-(4-pyridyl)hydrazine (LXXXIII), only 4-(*N*-monoalkylamino)pyridines (LXXXV) are formed and not even traces of *N*-monoalkylanilines can be detected:[94]



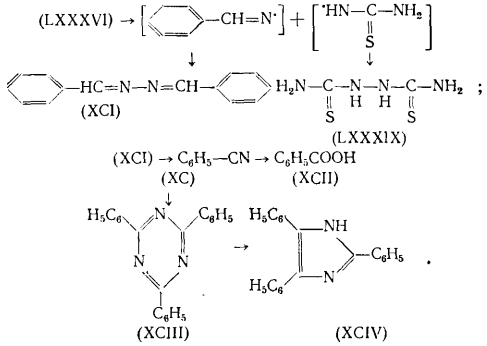
On passing to benzaldehyde thiosemicarbazone (LXXXVI),[97] the reaction with potassium ethoxide also proceeds via the general mechanism and *N*-ethylthiourea (LXXXVII) and the potassium salt of benzaldehyde oxime (LXXXVIII) are formed:



(LXXXVI) (LXXXVII) (LXXXVIII)

As in other analogous reactions, a thermal decomposition of the radical type takes place simultaneously with this process.

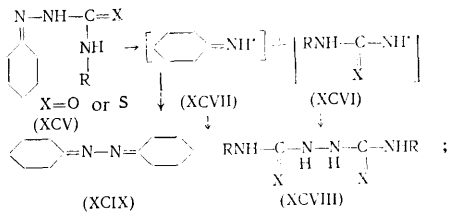
Radical reactions of benzaldehyde thiosemicarbazone (LXXXVI) led to the formation of hydrazodithioformamide (LXXXIX) and benzonitrile (XC) apparently via the benzylideneazine (XCI). On further treatment, the latter partly hydrolyses to benzoic acid (XCII) and, under the reaction conditions, trimerises partly to 2,4,6-triphenyl-1,3,5-triazine (XCIII), which recyclises to the thermally more stable 2,4,5-triphenylimidazole (XCIV):



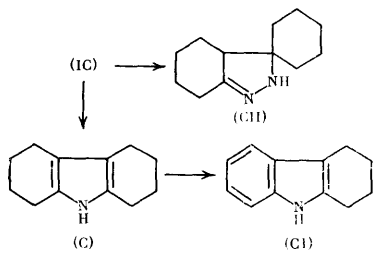
(XCIII) (XCIV)

Benzaldehyde semicarbazone proved to be much more stable and withstood heating with alkali metal alkoxides to 300 °C without any changes.[94,97]

When the semicarbazone (XCV, R = H, X = O), the phenylsemicarbazone (XCV, R = $C_6H_5$, X = O), and the thiosemicarbazone (XCV, R = H, X = S) of cyclohexanone[98,99] are treated with both alkali metal alkoxides and catalytic amounts of Lewis acids (zinc chloride or tin dichloride), reactions of the Fischer type do not occur and only homolytic dissociation of the N–N bond takes place. It is not accompanied by *N*-alkylation but leads to the *NN'*-diacylated hydrazines (XCVIII) and the cyclohexanone azine (XCIX) as a result of the recombination of the radicals (XCVI) and (XCVII) formed:



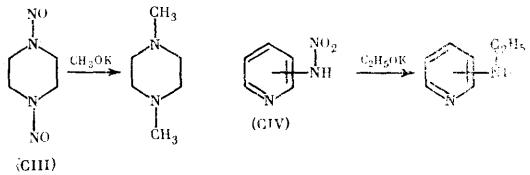
(XCV) (XCVII) (XCVI) (XCIX) (XCVIII)



(C) (CI)

[When R = Ph, the radical (XCVI) formed is stabilised as a result of its cleavage to aniline.] According to Kost and Grandberg,[100] cyclohexanone azine (XCIX) is readily converted further into octahydrocarbazole (C) and the product of its partial oxidation by atmospheric oxygen—tetrahydrocarbazole (CI) and also into 5,5-pentamethylene-3,4-tetramethylenepyrazoline (CII).

The increase in the polarity of the N–N bond as a result of conversion into the *N*-nitroso-derivative (CIII) and the *N*-nitroamino-derivative (CIV) facilitates the cleavage of the N–N bond with simultaneous *N*-alkylation on treatment with alkali metal alkoxides:[101,102]



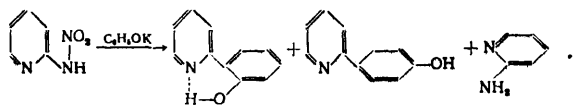
(CIII) (CIV)

The corresponding inorganic nitrites and nitrates are evidently formed as second components of these reactions.

It is of interest that in the case of the isomeric 2-, 3-, and 4-aminopyridines (CIV) the ease of dissociation of the N–N bond with simultaneous *N*-alkylation increases in the sequence 4 < 3 < 2, whereas the opposite sequence of reactivities is characteristic of the analogous isomeric pyridylhydrazones: 2 < 3 < 4.[102] Thus in the preparative synthesis of 3- and 4-monoalkylaminopyridines the best results are produced by the corresponding reactions of benzaldehyde 3- and 4-pyridylhydrazones with alkali metal alkoxides, while the interaction of 2-nitroaminopyridines with alkali metal alkoxides is a more convenient preparative synthetic method for 2-monoalkylaminopyridines.[102]

In contrast to N–N bond dissociation processes with simultaneous alkylation or benzylation, when the corresponding phenoxides are used in the reaction with 2-nitroaminopyridine instead of alkali metal alkoxides benzylates,

denitroamination and arylation in the 2-position in the pyridine ring are observed:[103]



## V. ELECTROCHEMICAL AND PHOTOCHEMICAL PROCESSES

The electrochemical and photochemical processes involving the dissociation of the N–N bonds examined in the previous review[1] also developed further during the last decade. It has been shown that, in contrast to the polarographic reduction of the hydrazones (CV) in aqueous alcoholic buffer solutions, which proceeds via the addition of four electrons to the protonated form with formation of amines,[104] in an aprotic medium [dimethylformamide] (DMF) the aryl hydrazones (CV) as well as the thiosemicarbazones or acyl hydrazones of aromatic aldehydes and aliphatic aromatic ketones initially undergo an electrode reaction involving the irreversible addition of one electron to the azomethine group with subsequent cleavage of the N–N bond:[105,106]

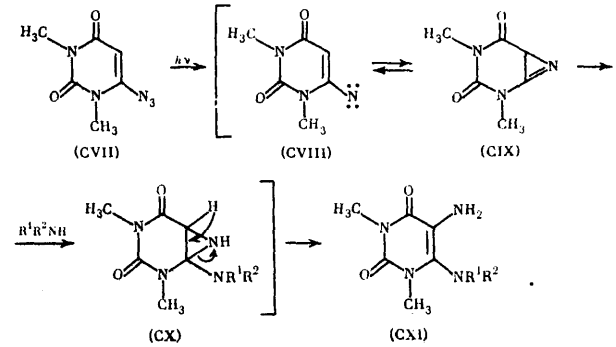
$$\underset{\text{(CV)}}{R'-NH-N=CH-R} \rightarrow \dot{N}=CHR + NH_2R' \quad .$$

The formation of the corresponding nitriles[107] or their radical-anions[109] as a result of the dissociation of the N–N bond has been demonstrated in relation to the electrochemical reduction of the disubstituted hydrazones of nitrobenzaldehyde and nitrofurfural in DMF. Aminonitrile cleavage has also been noted in the electrochemical reduction of *NN*-disubstituted hydrazones of benzaldehyde and benzoyl chloride (CVI) in an aprotic medium.[109] The following process mechanism has been proposed for the latter case:

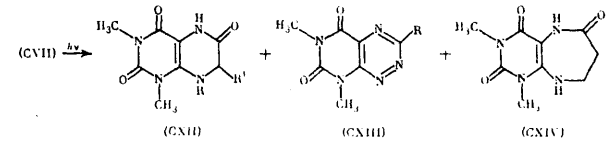
$$C_6H_5-\underset{\displaystyle Cl}{\underset{|}{C}}=N-N(C_6H_5)_2 \xrightarrow[-Cl^-]{+\bar{e}} C_6H_5\dot{C}=N-N(C_6H_5)_2 \xrightarrow{+\bar{e}} \bar{N}(C_6H_5)_2 + C_6H_5-CN \rightarrow$$
$$\xrightarrow{+\bar{e}} [C_6H_5-CN]^- \quad .$$
$$\text{(CVI)}$$

In further investigation of the mechanism of the electrochemical reduction of the aminonitrile cleavage of the hydrazone derivatives of nitrobenzaldehyde, it was established that the dissociation of the N–N bond is preceded by deprotonation, at the potentials of the second wave, of the initial depolariser by the dianion formed under these conditions. The mobility of the aldehyde hydrogen atom is then determined by many factors (the basicity, the character of the electronic polarisation of the hydrazone fragment, and the polarity of the N–N bond), discovered in a study of the $^1H$ NMR spectra and the absorption spectra of the electrochemical oxidation of the substrate at a graphite electrode and justified by quantum-chemical calculations.

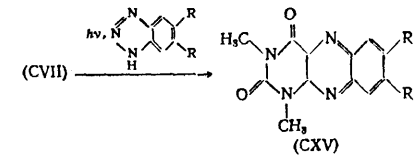
In the course of the development of the previous studies on the photolysis of various azides,[1] the photochemical reactions of 6-azido-1,3-dimethyluracil (CVII) in the presence of various primary and secondary amines have been investigated during the last decade.[111] The above reactions apparently proceed via the intermediate formation of the nitrene (CVIII) with subsequent appearance of the intermediate azirine (CIX). The nucleophilic addition of alkylamines to compound (CIX) and the electrocyclic opening of the aziridine ring (CX) formed complete the synthesis of 6-alkylamino-5-amino-1,3-dimethyluracils (CXI):



Analogous photochemical cleavage reactions of the azides (CVII) with dissociation of the N–N bond, the appearance of the energetically favourable nitrogen molecule, and the formation of a nitrene which undergoes further reactions[112] constitute the basis of the interaction of compound (CVII) with α-aminoacid esters. The final products of these photochemical reactions are lumazines—derivatives of pyrimido(4,5-*b*]-pyrazine (CXII):

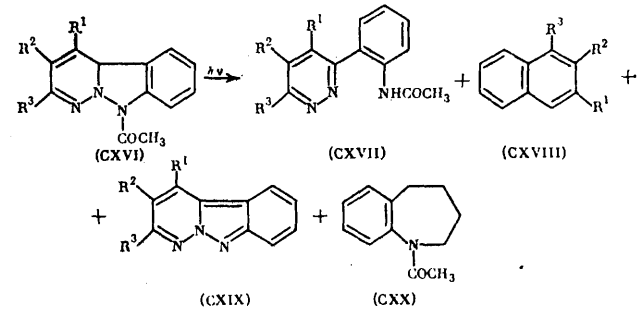


Further development of this method using acylhydrazines as the amine components has led to the synthesis of 7-azalumazines (fervenulins) (CXIII),[111,113] while derivatives of pyrimido[4,6-*b*]diazepines (CXIV) have been obtained from β-aminoacid esters [111] and fervenulins (CXIII) and alloxazines (CXV) have been obtained from tetrazoles and benzotriazoles:[114]



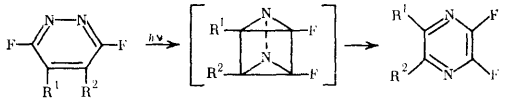
The above reactions are accompanied by the dissociation of the N–N bonds not only in the azide group but also in the cyclic tetrazole (or corresponding benzotriazole) system.

Interesting photochemical reactions with cleavage of the N–N bond have been observed for cyclic 1,3-adducts of *N*-acetyliminopyridazinium ylides with dehydrobenzene (CXVI).[115,116] The photolysis of the corresponding 3-alkoxy-derivatives (CXVI, $R^3$ = O-alkyl) proceeds with dissociation of the N–N bond and aromatisation accompanied by the formation of 3-(2-acetamidophenyl)pyridazine (CXVII) together with the product of the elimination of molecular nitrogen (acetylnitrene) and subsequent aromatisation [alkoxynaphthalene (CXVII)] as well as the *N*-deacylated aromatic product (CXIX):[116]



The 3-methyl derivative (CXVI), $R^3 = CH_3$, is in the main converted into the *N*-deacetylated aromatic product (CXIX), while compound (CXVI, $R^3 = H$), unsubstituted in the pyridazine ring, is converted into *N*-acetylbenzazepine (CXX) with elimination of molecular nitrogen.[116]

UV irradiation of the tetrafluoropyridazine (CXXI, $R^1 = R^2 = F$) and of its perfluoroalkyl derivatives in the gas phase leads to the corresponding perfluoropyrazines (CXXIII) via the formation of the intramolecular valence isomers of the type of perfluoro-1,2-diazabicyclo[2.2.0]hexa-2,6-diene (CXXII):[117,118]



(CXXI) (CXXII) (CXXIII)

Thus the new studies on the dissociation of the N–N bond have significantly extended the theoretical ideas and preparative possibilities in organic chemistry.

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# Alkyl Orthoesters and Their Applications in Organic Synthesis

L.A.Pavlova, Yu.A.Davidovich, and S.V.Rogozhin

A systematic account is given of data characterising the chemical properties of alkyl esters of orthocarboxylic acids. The suggested reaction mechanisms are discussed and the extensive possibilities of the application of the orthoesters in the solution of various problems in organic synthesis are demonstrated.
The bibliography includes 91 references.

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## I. INTRODUCTION

Inspection of the literature data of recent years shows that the interest in orthoesters, which are reactive chemical reagents, has not weakened and has stimulated the discovery of further new aspects of the application of these compounds. The aim of the present review is to give a systematic account of the data concerning the use of alkyl orthoesters in organic synthesis, which have been published during the period from 1971 to 1984 and which have not been included in earlier reviews.[1-6]

One of the fundamental works devoted to the synthesis and properties of orthoesters and their analogues is the book by De Wolfe[1] in which a profound analysis of all possible chemical reactions of orthoesters, thio-orthoesters, amidoacetals, ester-aminals, and orthoamides has been carried out and the proposed reaction mechanisms are discussed. A review by the same author, with an extensive coverage of the methods of synthesis of orthoesters, was published somewhat later.[2] One of the chapters in Bergstrom's book[3] is devoted to the chemistry of orthoesters, acetals, and ketals, attention being concentrated on the methods of synthesis of orthoesters and the mechanism of their hydrolysis.

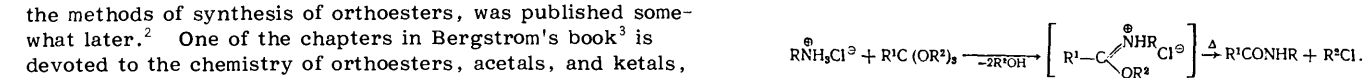
The Soviet literature on the synthesis and properties of orthoesters is represented by two reviews[4,5] and the chemistry of cyclic orthoesters is described in a collected volume.[6]

Since the modern methods of synthesis of orthoesters have been described in the above literature sources in adequate detail, the data on the hydrolysis of orthoesters have been analysed, and the data concerning the synthesis and behaviour of cyclic orthoesters have been surveyed, this review does not include the relevant sections.

## II. INTERACTION OF ORTHOESTERS WITH NITROGEN-CONTAINING COMPOUNDS

### 1. Reactions with Primary and Secondary Amines

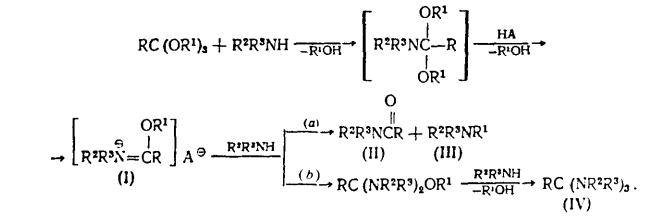
It has been shown[7] that alkyl orthoesters can be used successfully for the acylation of primary and secondary amines and aminoacid esters. The reaction is carried out by heating briefly (70–90 °C) the amino-component in the form of the hydrochloride (or another salt) with the alkyl orthoester. An alcohol, an alkyl halide, and the corresponding *N*-acyl derivative of the amino-component, whose yield in most cases exceeds 90%, are then formed. The nature of the products obtained suggests that the reaction takes place mainly via a stage involving the formation of imidoester salts, which undergo the "Pinner" cleavage to the amide and the alkyl halide at elevated temperatures:



It is noteworthy that the mechanism of the interaction of orthoesters with amides depends in most cases on whether the amino-group is in the free state or whether the salt of the amino-component is introduced into the reaction; it also depends on whether the salt has been formed with a weak or a strong acid.

It is known[1] that the acid-catalysed reactions of secondary amines with orthoesters can lead to the formation of three types of products: amidoacetals, ester-aminals, and orthoamides. The interaction of orthoesters with secondary amines of different types has been investigated in order to

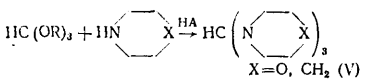
discover a convenient method for the synthesis of ortho-amides.[8] It was shown that the yield of the latter depends mainly on the reactivity and structure of the initial amine and also on the type of the acid catalyst used in the reaction. For example, when weakly basic amines, such as *N*-alkylanilines, are acted upon by orthoesters, then orthoamides are either not formed at all (both in the absence of catalysts and in the presence of toluene-*p*-sulphonic acid) or are obtained in a low yield (in catalysis by hydrochloric or acetic acid). In the presence of acids the reaction can proceed via the following mechanism:



The changes in the ratios of the products (II), (III), and (IV), obtained in the presence of different acids have been explained[8] by the influence of the anion $A^-$ on the structure of the intermediate complex (I).

The main products of the reactions of orthoformates with alkylanilines are *N*-alkylformanilides (II) and *NN*-dialkylanilines (III). *N*-Benzylmethylamine behaves analogously to *N*-alkylanilines, affording approximately equal amounts of *N*-benzyl-*N*-methylformamide and *N*-benzyl-*N*-ethylmethylamine in the reaction with triethyl orthoformate in the presence of toluene-*p*-sulphonic acid.

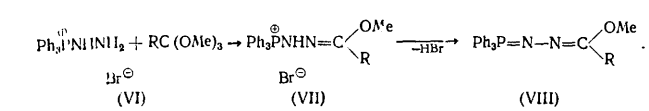
Acyclic secondary amines do not form appreciable amounts of orthoamides in their reactions with orthoesters under these conditions. Only the interaction of orthoesters with highly basic cyclic amines, such as morpholine, piperidine, and *N*-methylpiperazine led to the isolation of the corresponding orthoamides (V) in high yields regardless of the type of catalyst employed:



This method of synthesis of the orthoamides (V) is more convenient and more economical than those used previously,[9,10] although it does suffer from certain limitations: orthoamides are formed only from six-membered cyclic amines; it has not been possible to carry out similar reactions with pyrrolidine and hexamethyleneimine.

## 2. Reactions with Compounds Containing the Hydrazino-Group

The interaction of orthoesters with hydrazinotriphenylphosphonium bromide (VI) leads to a new method of synthesis of *syn*- and *anti*-α-methoxyalkylidenetriphenylphosphazines (VIII).[11] The attack by the orthoester on the hydrazino-group of the initial compound (VI) results in the formation of α-methoxyalkylidenetriphenylphosphazinium bromides (VII), which can be readily converted into the corresponding phosphazines (VIII) via dehydrobromination:

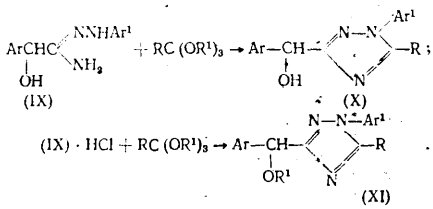


The thermal or photochemical decomposition of compound (VIII) leads to the formation of α-alkoxycarbenes, which have been little investigated hitherto.

## 3. Reactions with Amino-components Accompanied by Cyclisation

Alkyl orthoesters are finding increasing applications in the synthesis of a wide variety of heterocyclic derivatives. The reaction involving the formation of triazoles from orthoesters and aryl-substituted hydrazones of carboxylic acids has been known for a long time.[12] Studies on the mechanisms of the analogous reactions and side processes are being continued.

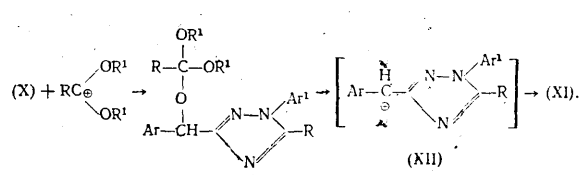
It has been shown[13] that the reactions of alkyl orthoesters with the *N*-arylamidrazones of mandelic acid (IX) (in the form of a free base) lead to the formation of 1,3,5-trisubstituted triazoles (X), the hydroxy-group in the side chain remaining unchanged. If the hydrochloride of the amidrazone (IX) is used as the initial compound, the corresponding triazole (XI) with an alkylated hydroxy-group is obtained:



The corresponding monochloro-compound (IXa, Ar = *o*-$C_6H_4Cl$) reacts with the orthoester, both in the form of a free base and in the form of a hydrochloride, to form only a triazole of type (X) with an unsubstituted hydroxy-group.

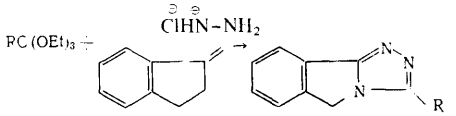
Under the influence of acid (HCl), the orthoesters are apparently converted into the corresponding dialkoxycarbonium ions, which are known to be strong alkylating agents. In the presence of acids, the hydroxy-group in the side chain of triazole is therefore alkylated, while in the absence of acid it remains unaltered. This hypothesis has been confirmed by the fact that the product (X) is converted quantitatively into compound (XI) in solutions of orthoesters after the addition of acids. The monochloro-derivative (IXa) is not alkylated, probably owing to steric factors.

The same workers[14] traced analogous reactions of the optically active *N*-arylamidrazones of mandelic acid in the presence and absence of inorganic acids. In the absence of acids, the reaction proceeds stereospecifically: the dextrorotatory amidrazone forms a dextrorotatory triazole. The reactions with the hydrochlorides of the optically active amidrazones result in the formation of a racemic triazole alkylated at the hydroxy-group. It has been suggested that, as a result of the attack on the hydroxy-group of triazole by the dialkoxycarbonium ion, the cation (XII) is formed as an intermediate. Further reactions of this cation lead to the racemate (XI):



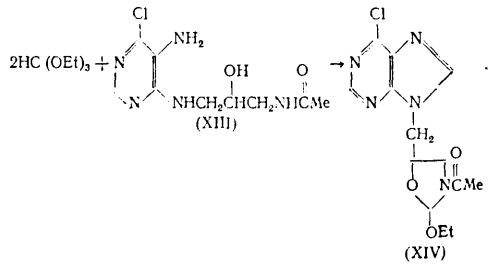
In certain cases the reaction between the orthoester and the amino-component is possible only in the presence of acid. For example, the reaction of ethyl orthoacetate or ethyl

orthoformate with the hydrochloride of 1-hyrazinoisoindolenine proceeds solely as a result of the formation of dialkoxycarbonium ions.[15] Its product is a triazoloindole:



In the absence of acid, the orthoesters are passive in relation to hydrazinoisoindolenines.

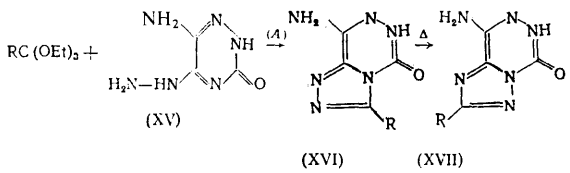
It is known that, on reaction with 5-amino-4-hydrazinopyrimidines, the orthoesters give rise to *N*-aminoimidazolopyrimidines.[16] The reaction between orthoformate and diaminopyrimidine (XIII) is of the same type:[17]



(XIII) (XIV)

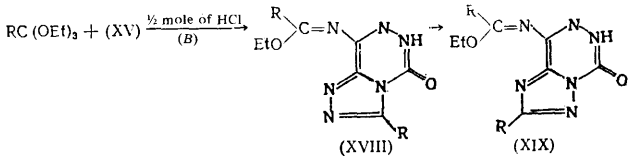
However, four active groups of the initial compound (XIII) participate simultaneously in this reaction, which results in the formation of two new rings: the imidazole and oxazolidine rings. The disubstituted purine (XIV) formed is used as the intermediate in the synthesis of an acyclic analogue of puromycin.

The reaction of orthoesters with 6-amino-5-hydrazino-1,2,4-triazin-3-one (XV) does not take place unambiguously.[18] The course of this reaction is influenced by several factors: the temperature conditions, the presence of acid in the reaction mixture, and even its amount. It is noteworthy that, at room temperature in the absence of acid, the orthoesters do not interact with compound (XV). When the orthoesters are refluxed with compound (XV) without added acid [version (*A*)], cyclisation takes place initially with formation of compound (XVI), the primary amino-group not being involved. Subsequently, as a consequence of an intramolecular rearrangement, the product (XVI) is converted into the more stable compound (XVII):



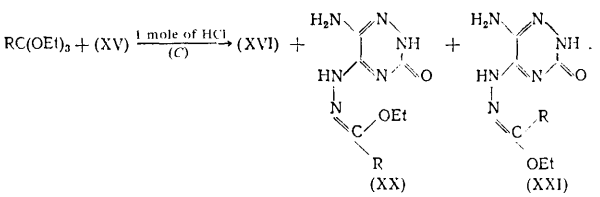
(XV) (XVI) (XVII)

At room temperature in the presence of a certain amount of hydrochloric acid [version (*B*)], a mixture of products (XVIII) and (XIX) was obtained. It was noted that compound (XVIII) gradually isomerises to compound (XIX):



(XVIII) (XIX)

When the reaction was carried out without heating in the presence of an equimolar amount of acid [version (*C*)], three products were isolated: (XX), (XXI), and (XVI). The quantitative stereoisomer ratio (XX):(XXI) in the mixture was 2:1:



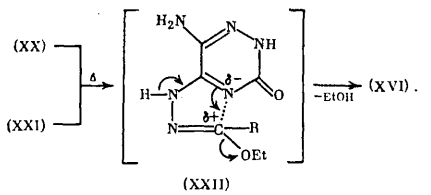
(XX) (XXI)

If more than one equivalent of hydrochloric acid is introduced into the mixture of the initial reactants at room temperature [version (*D*)], then only the product (XVII) is obtained.

In contrast to other orthoesters, orthoformate reacts with the initial compound (XV) to form products of type (XVI) and (XVII) regardless of whether the acid is present in an excess or deficiency.

We shall now consider the proposed reaction mechanism.

*Version* (*A*). In the absence of acid, the reaction mixture must be heated for the reactants to react. The orthoester molecule reacts with the hydrazino-group of compound (XV) as the most reactive nucleophilic centre. This results in the initial formation of the products (XX) and (XXI), which cyclise with simultaneous elimination of an alcohol [transition state (XXII)]. Heating promotes the occurrence of this process, which ultimately leads to the formation of compound (XVI):



(XXII)

*Version* (*B*). When concentrated hydrochloric acid is introduced into the reaction mixture, more active electrophiles, dialkoxycarbonium ions, appear in the reaction sphere. They can apparently interact not only with the hydrazino-group but also with the less reactive, in the given instance, amino-group of the initial compound (XV). The products of this reaction are compounds (XVIII) and (XIX).

Thus, in the presence of acid, which plays the role of a catalyst and reactant, there is a possibility of the occurrence of a series of competing reactions: non-ionic interaction between the orthoester and the initial compound (XV); the reaction of the amino-component with the acid; the interaction of the orthoester with the acid; the attack by dialkoxycarbonium ions on the active groups in the initial and intermediate compounds; acid-catalysed cyclisation reactions.

Presumably the products of the substitution in the amino-group of type (XVIII) and (XIX) are not formed in versions (*C*) and (*D*) as a consequence of the protonation of the amino-group of the initial compound (XV).

In the presence of an excess of acid in the reaction mixture, compounds (XX) and (XXI) were not detected apparently because in the presence of acid their conversion into the bicyclic product (XVI) is facilitated.

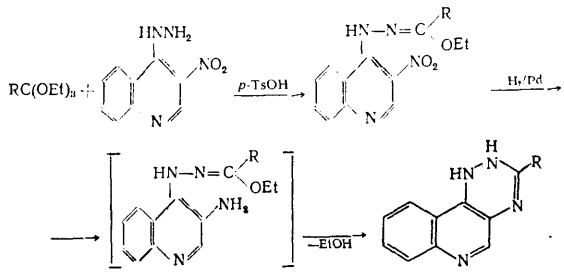
The anomalous behaviour of orthoformate can apparently be accounted for by the fact that the cations $HC^{\oplus}(OR)_2$ formed as a result of its interaction with the acid are least stable in the series of dialkoxycarbonium ions. For this reason, non-ionic processes leading to the formation of compounds

(XVI) and (XVII), which are also formed without the addition of acid, can predominate in the reactions of orthoformate. Compounds of type (XX) and (XXI), where R = H, could be formed as intermediates, but they cyclise to compound (XVI) more readily than others, which follows from the examination of the transition state (XXII).

The study of Lovelette and Geagan[18] clearly demonstrated how significant is the alteration of conditions in the reaction between orthoesters and polyfunctional amino-components.

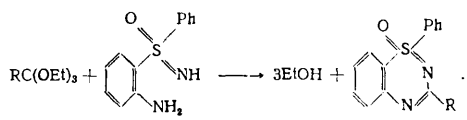
Compounds (XXIII), possessing anti-inflammatory activity greatly exceeding that of acetylsalicylic acid, have been obtained from alkyl orthoesters and 4-hydrazino-3-nitroquinoline.[19]

The first stage represents a typical interaction of an alkyl orthoester with the hydrazino-group of the initial quinoline catalysed by toluene-p-sulphonic acid. On hydrogenation in the presence of palladium, the nitro-group is reduced to the amino-group, as a consequence of which intermolecular cyclisation becomes possible:

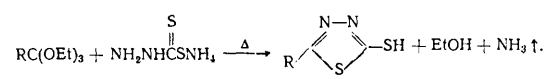


(XXIII)

New cyclic sulphoximides have been obtained by the reaction of orthoacetates (and orthoformates) with *S*-(*o*-aminophenyl)-*S*-phenylsulphoximide:[20]



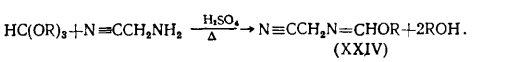
Five-membered thiadiazole rings, containing the mercapto-group in the side chain, can be conveniently obtained by refluxing orthoesters with salts of *N*-aminodithiocarbamic acid:[21]



Because of the wide variety of the products obtained, the reaction between orthoesters and aminonitriles are of undoubted interest.

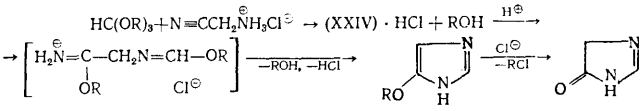
A fundamentally new approach to the methods of synthesis of 5-imidazolones has been described.[22] It is based on the interaction of orthoesters with aminoacetonitrile.

The reaction between orthoformate and aminoacetonitrile has its characteristic features. If the interaction is carried out in the presence of catalytic amounts of sulphuric acid with simultaneous removal of the alcohol, then alkyl *N*-cyanomethylacetimidate (XXIV) is obtained in a high yield:



(XXIV)

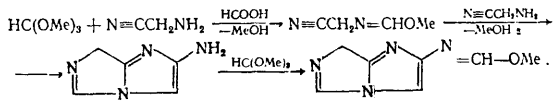
When the orthoester is made to react with the hydrochloride of aminoacetonitrile, the only product is 5-imidazolinone (XXV) (yield in excess of 90%). According to the authors' hypothesis,[22] the product (XXIV) is formed initially, its nitrile group undergoing acid-catalysed (HCl) alcoholysis. This is followed by cyclisation to 5-alkoxy-1*H*-imidazole and the latter is converted, after being attacked by the halide ion, into the 5-imidazolinone (XXV) with elimination of the corresponding alkyl halide:



(XXV)

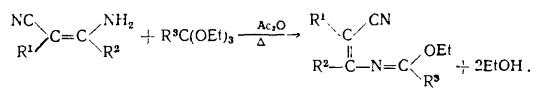
This method ensures a high yield of compound (XXV) and is simpler and more convenient in practice than the earlier procedures.[23,24]

Trimethyl orthoformate taken in excess reacts differently with aminoacetonitrile in the presence of catalytic amounts of formic acid. The reaction proceeds in several stages and the final product is methyl *N*-{7*H*-imidazo[1,5-*a*]-imidazol-2-yl acetimidate (XXVI), isolated in 24% yield:



(XXVI)

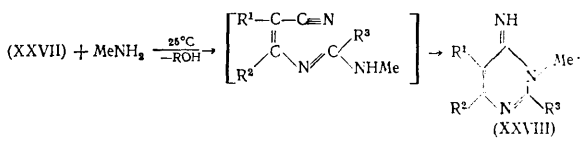
Orthoesters combined with enaminonitriles proved to be the best reagents for the synthesis of *C*-alkylated 1,6-dihydro-6-imino-1-methylpyrimidines (XXVIII).[25] The reaction of the orthoester with an enaminonitrile gives rise to the corresponding ethoxyalkylidene derivative (XXVII):



(XXVII)

The reaction proceeds, as with aminoacetonitrile, in the absence of acids[22] with the sole difference that here there is a possibility of the formation of the *cis*- and *trans*-isomers, depending on the structure of the initial enaminonitrile.

By treating compound (XXVII) with an alcoholic solution of methylamine, it is easy to achieve the substitution of ethoxy-groups. This reaction is accompanied by spontaneous cyclisation to the pyrimidine (XXVIII):



(XXVIII)

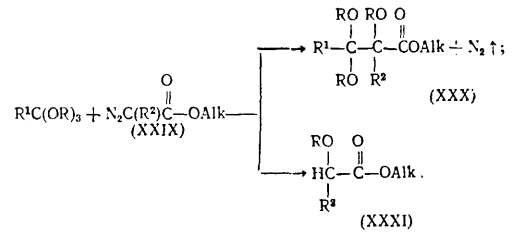
Derivatives of this type were previously difficult to obtain.[26] They are of interest as convenient objects for the study of the mechanism of the Dimroth rearrangement.[25]

A number of reactions involving orthoesters and amino-components of different types (amines, amides, and carboxylic acid amidrazones) have been examined in a book.[27]

## 4. Reactions with Diazo-compounds

Alkyl orthoesters, particularly orthoformate, orthoacetate, and orthopropionate, readily react with diazo-compounds (XXIX).[28] The reaction is catalysed by Lewis acids:

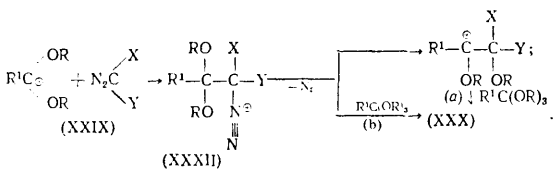
copper(II) trifluoromethanesulphonate, rhodium tetra-acetate, and boron trifluoride etherate:



(XXIX) (XXX) (XXXI)

The reactions led to the isolation of the main product (XXX) and the side product (XXXI). Neither the reaction time nor the amount of catalyst affected the yield of the main product (XXX) and only the nature of the catalyst employed was found to be important. When copper(II) trifluoromethanesulphonate or boron trifluoride etherate are used, the amount of side product (XXXI) is small.

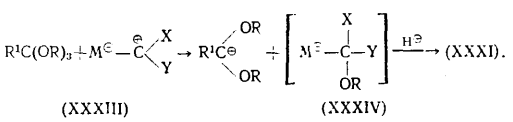
It has been suggested[28] that the catalysts enumerated, bound in a complex with the diazo-component, promote the formation of a dialkoxycarbonium ion, which is itself an active reagent. It adds to the diazo-derivative, after which nitrogen is eliminated and the product (XXX) is formed:



(XXIX) (XXXII) (XXX)

When nitrogen is split off from the intermediate (XXXII), a new electrophilic centre to which the alkoxy-group can migrate (*a*) or the usual substitution of the diazonium group takes place (*b*), is probably formed.

The product (XXXI) becomes the main one if transition metal compounds are used as catalysts. The transition metal and the diazo-component apparently form a dipolar carbene complex (XXXIII), to the electrophilic centre of which the alkoxy-group of the orthoester can be transferred, as a result of which one obtains the dialkoxycarbonium ion and the active complex (XXXIV). When a proton is captured by the complex (XXXIV), the product (XXXI) is formed with dissociation of the carbon–metal bond:



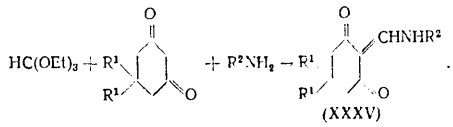
(XXXIII) (XXXIV) (XXXI).

## III. THREE-COMPONENT CONDENSATIONS

One of the most promising applications involves the use of orthoesters in three-component condensation reactions. The high reactivity of orthoesters and the numerous varieties of reagents employed in these reactions create a unique possibility for the synthesis of new structures. The mechanism of the three-component condensation has been described in a general form and discussed in detail in a review.[4]

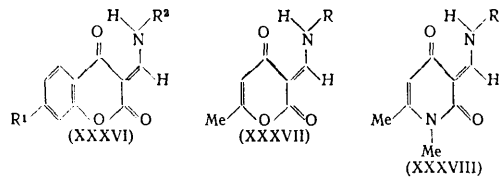
A number of studies[29–32] have been devoted to reactions in which alkyl orthoesters interact simultaneously with a carrier of an active methylene group and a carrier of an amino-group. A convenient method of synthesis of an extensive class of compounds, namely acyl- and diacyl-enamines, is based on this reaction.

For example, orthoformates readily react with cyclohexane-1,3-diones and aromatic amines to form the corresponding enaminodiketones (XXXV), which can in their turn be converted into hexahydroquinolinediones:[29]



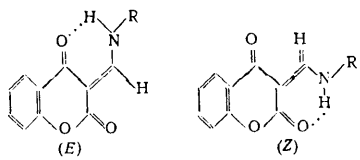
(XXXV)

Thus 3-anilinomethylenechroman-2,4-diones (XXXVI), 3-anilinomethylene-6-methyl-2,3-dihydropyran-2,4-diones (XXXVII), and 3-anilinomethylene-1,6-dimethyl-2,3-dihydropyridine-2,4-diones (XXXVIII) have been obtained from orthoformates, anilines, and cyclic six-membered 1,3-diketones of more complex structure:[30]



(XXXVI) (XXXVII) (XXXVIII)

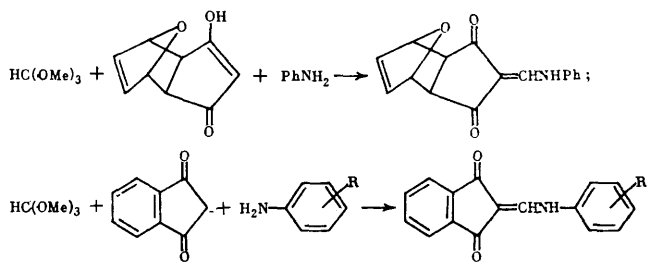
Probably by virtue of steric factors, only orthoformate can react with six-membered diketones and aromatic amines. It has been shown[30] that the reaction products consist of a mixture of stereoisomers:



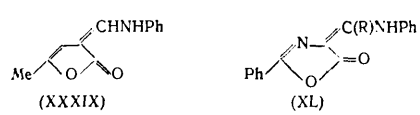
(*E*) (*Z*)

The use of five-membered cyclic 1,3-diketones in the three-component condensation also proved to be successful.[31] In this version it is possible to employ aliphatic primary amines as well as aromatic amines.

Condensed systems can also serve as the methylene components. The only important factor is that the active methylene group should belong to a five-membered ring. The following reactions proceed smoothly:[31]



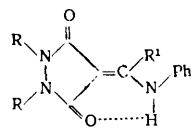
Compounds (XXXIX) and (XL), each of which can be resolved into geometrical isomers with the aid of fractional crystallisation, have also been obtained:[31]

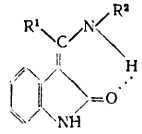


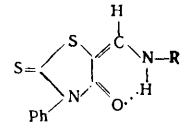
(XXXIX) (XL)

The derivatives (XLI) and (XLII) have been synthesised with participation of orthoacetate and orthopropionate. It has

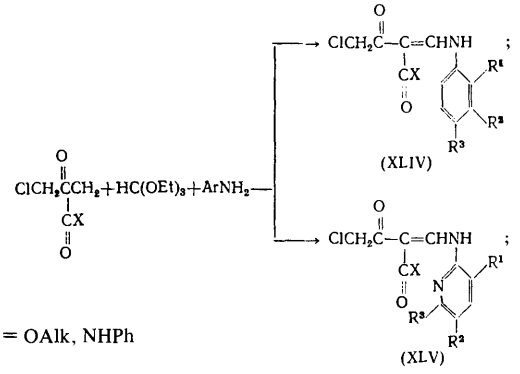
been noted that compound (XLII) has cytotoxic properties:[31]


(XLI)


(XLII)


(XLIII)

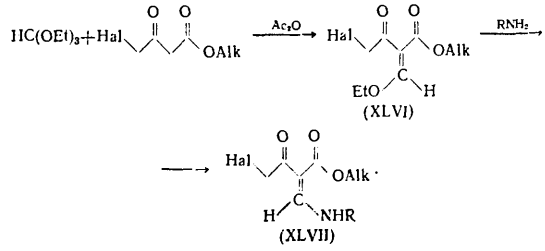
Compounds (XLIII) are obtained by the interaction of orthoformates with aliphatic amines and *N*-phenylrhodanine at an elevated temperature (150 °C).[31] Alkyl γ-halogenoacetoacetates can be used successfully in three-component condensation subject to the condition that their reaction partners are orthoformate and aromatic amines.[32] The derivatives (XLIV) are then obtained from anilines and compounds (XLV) are obtained from 2-aminopyridines, both in the form of mixtures of *E*- and *Z*-isomers:


X = OAlk, NHPh

(XLIV); (XLV)

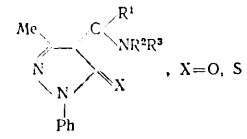
Compounds (XLIV) and (XLV) are used as intermediates in the synthesis of derivatives of 3-hydroxypyrroles, pyrido-1,2-pyrimidones, and quinolines.[32]

The three-component condensation of orthoesters, halogenoacetoacetates, and aliphatic amines is complicated by side reactions.[32] For this reason, the corresponding derivatives of *N*-alkylaminomethylene-γ-halogenoacetoacetic acid (XLVII) can be more conveniently obtained in two stages. The orthoformate is initially made to react with the methylene component in the presence of acetic anhydride, which leads to the formation of the ethoxymethylene derivatives (XLVI). The latter are treated with aliphatic amines and the required product (XLVII) is isolated:

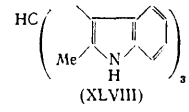

(XLVI); (XLVII)

Thus it has been demonstrated clearly by means of a number of examples that the method of synthesis of ββ-diacylenamines and their analogues via a type of three-component condensation has advantages over previous procedures.[33–35] In the vast majority of cases it consists of a single stage, is carried out under mild conditions, and there is only one side product, an alcohol, which can be readily removed from the reaction mixture.

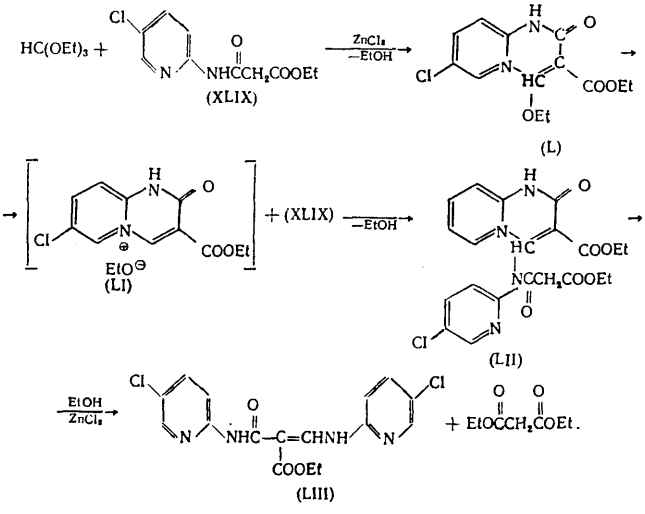
The choice of methylene components is not limited to carbonyl derivatives. Together with alkylaminomethylene-5-pyrazolinones, their thio-analogues have been obtained by the method of three-component condensation:[31]


, X=O, S.

Some of the methylene components tested under the conditions of three-component condensation behaved anomalously. For example, 1-indanone and 2-methylindole reacted with orthoformate without the participation of the amino-component, to form products of type (XLVIII):[31]

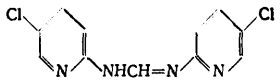

(XLVIII)

The interaction of orthoesters with polyfunctional compounds can proceed via a mechanism of the type of three-component condensation. For example, in the reaction with orthoformic ester, one molecule of 2-ethoxycarbonylacetamidopyridine (XLIX) behaves as the methylene component, while the other behaves as the amino-component.[36] The authors suggest that this reaction mechanism can be represented schematically as follows:

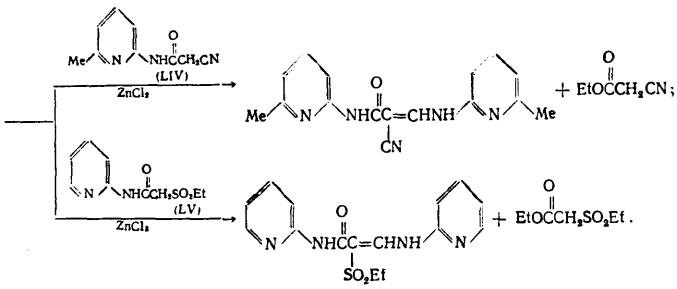

(XLIX); (L); (LI); (LII); (LIII)

The configuration of compound (L) is such that, under the influence of the electronegative nitrogen atom of the pyridine ring on the nearest ethoxy-group, the elimination of the latter in the form of the corresponding anion is facilitated. An active ionic compound (LI), which can react with the amide nitrogen atom of the initial compound (XLIX), is formed under these conditions. The product (LII) obtained undergoes alcoholysis under the influence of the alcohol, formed as a side product under the conditions of catalysis by zinc chloride, malonic ester being split off. Compound (LIII) is obtained in this way. In order to increase the yield of compound (LIII) from 24% to 41%, it was found to be sufficient to replace the acetic anhydride, normally employed as the solvent in such reactions, by ethyl alcohol.[36]

The reaction of 2-amino-5-chloropyridine with orthoformate is of the same type, the product being a formamidine:[36]



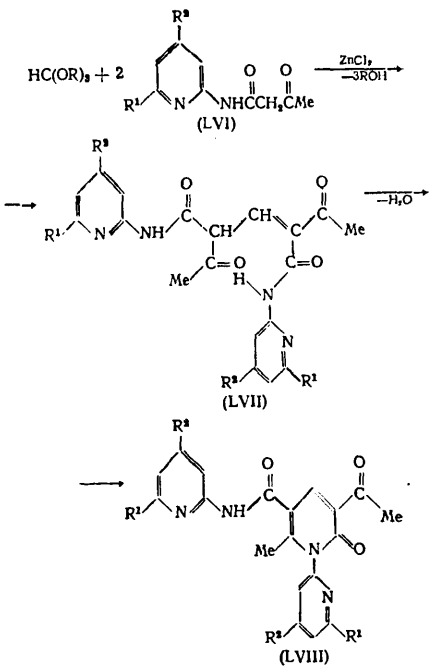
When the corresponding cyanoacetyl derivative (LIV) and the ethanesulphonylacetyl derivative (LV) were introduced into the reaction with the orthoester instead of the ethoxycarbonyl derivative, analogous products were obtained, although the yield of the main product in these cases was low (18–29%):



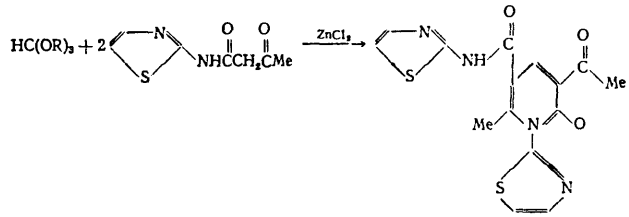
## IV. REACTIONS OF ORTHOESTERS WITH COMPOUNDS CONTAINING AN ACTIVE HYDROGEN ATOM

### 1. Interaction of Orthoesters with CH Acids

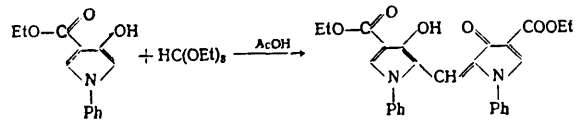
Certain reactions of this type lead to unexpected results. For example, when orthoformates interact with substituted 2-acetoacetylaminopyridines (LVI) in the presence of zinc chloride, complex tricyclic products (LVIII) are obtained.[37] Two molecules of the initial compound (LVI), which functions as the methylene component, react with a molecule of the orthoformic ester. The carbonyl and amide group approach one another so much in compound (LVII) that, under the catalytic influence of zinc chloride, intramolecular condensation takes place with elimination of a water molecule and formation of the pyridone ring (LVIII):



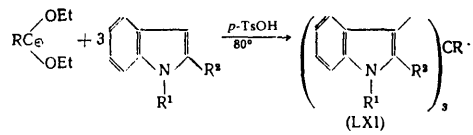
The interaction of orthoformate with 2-acetoacetylaminothiazole takes place analogously:[37]



The reaction of triethyl orthoformate with 3-hydroxy-4-ethoxycarbonyl-1-phenylpyrrole [32] leads to a compound containing the hydroxypyrrole and pyrrolinone groups:



Derivatives of indole are typical representatives of CH acids. The behaviour and reactivity of orthoesters in reactions with disubstituted indoles in the presence of organic acids have been investigated[38] and it has been shown that alkyl orthoesters participate in this reaction in the form of the corresponding dialkoxycarbonium ions, which attack the 3-position, where the electron density is highest, to form tri-indolylmethanes:



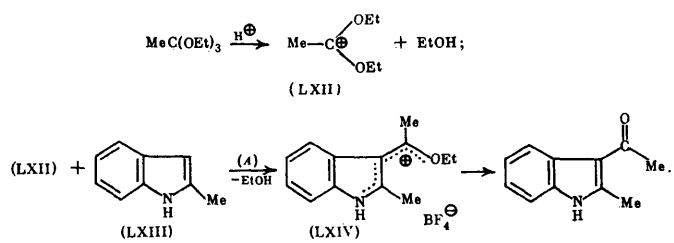
(LIX): R=H;
(LX): R=Me

Kinetic data have shown that the behaviour of the carbonium ions (LIX) and (LX) in reactions of this type is approximately the same, trimethoxycarbonium ions proving to be the least reactive.

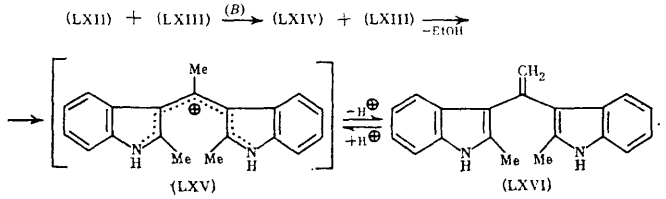
Reactions in which analogous products (XLVIII) were obtained by the interaction of 2-methylindole with orthoesters in the presence of organic bases were considered above; unfortunately the reaction mechanism was not discussed by Wolfbeis.[31]

By altering the reaction conditions, it is possible to obtain different products of the reaction of orthoesters with 2-substituted alkylindoles. A convenient method of synthesis of the pharmacologically active indolylcarbazole (LXVII) from ethyl orthoacetate and 2-methylindole has been proposed.

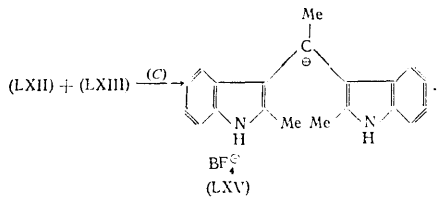
If the reaction between triethyl orthoacetate and 2-methylindole (LXIII) is carried out in methylene chloride in the presence of $HBF_4$ at 0 °C [version (*A*)], then the main product is 1-ethoxy-1-(2-methylindol-3-yl)ethyl tetrafluoroborate (LXIV). This relatively stable salt has been isolated in 46% yield. In aqueous organic media, it is gradually converted into 3-acetyl-2-methylindole.



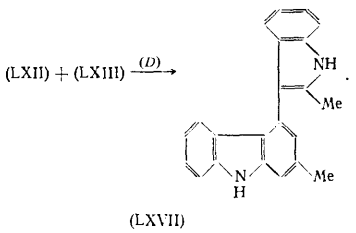
When the starting materials are refluxed in methanol in the presence of catalytic amounts of concentrated sulphuric acid [version (*B*)], the bisindolyl derivative (LXVI) is formed. The product (LXIV) formed initially apparently reacts under these conditions with yet another molecule of the initial indole (LXIII) and the intermediate bisindolylcarbonium ion (LXV) is converted on deprotonation into 1,1-bis(2-methylindol-3-yl)ethylene (LXVI) (yield 37%):




The cation (LXV) was isolated directly in the form of the tetrafluoroborate salt. For this purpose, the initial indole (LXIII) was activated with a Grignard reagent, namely ethylmagnesium bromide, and was then made to react with the orthoester in the presence of boron trifluoride [version (*C*)], the yield being 19%:




Under more severe conditions, after prolonged refluxing of the reactants in acetic acid or methanol in the presence of concentrated sulphuric acid [version (*D*)], 2-methyl-4-(2-methylindol-3-yl)-9*H*-carbazole (LXVII) is formed:

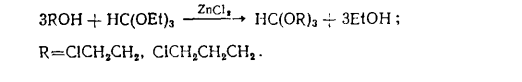



## 2. Reactions with Alcohols and Mercaptans

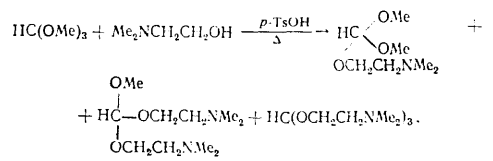
The reactions of alkyl orthoesters with alcohols have been investigated in fair detail.[1,2,4-6] They consist in the exchange of the alkoxy-group of the orthoesters with the corresponding alcohol residue. Using certain polyfunctional alkanols, it is possible to introduce additional active groups into the orthoester molecule. For this purpose, alkyl orthoesters are made to react with chloroalcohols, aminoalcohols, alkylaminoalcohols, and ethylenecyanohydrin.[40]

One, two, and three alkoxy-groups of the orthoester can exchange for the *O*-alkyl group of the alcohol depending on the structure of the latter and the reaction conditions (molar reactant ratio and the character of the catalyst employed). The reaction usually results in the formation of a mixture of products of similar structure, which makes it difficult to separate them.

Individual products have been obtained from ethyl orthoformate and ethylenechlorohydrin and also 3-chloropropanol in the presence of zinc chloride as the catalyst:



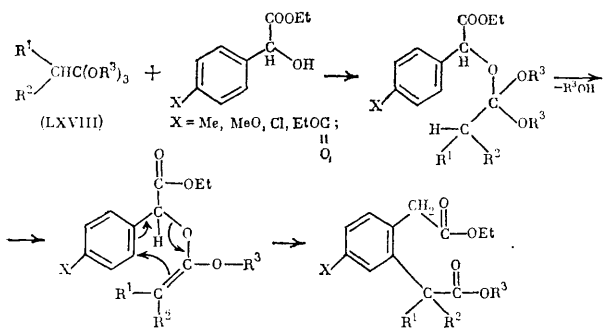

When orthoesters react with aliphatic aminoalcohols in the presence of acid catalysts (toluene-*p*-sulphonic acid, zinc chloride, or tin chloride), mixtures of mono-, di-, and trisubstituted aminoalkyl orthoesters are obtained and are separated by fractional distillation,[40-43] for example:




The mechanism of the interaction of orthoesters with unsaturated alcohols is much more complex, since reactions of this kind are usually accompanied by intramolecular rearrangements of the type of the Claisen rearrangement.[1,44-49,51,52]

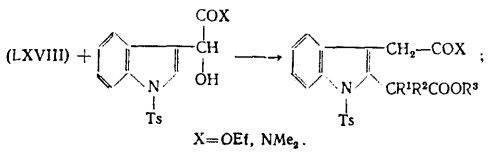
A series of studies[44-46] have been devoted to the mechanism of the interaction of orthoesters with aromatic derivatives containing a hydroxy-group in the α-position in the side chain.

A convenient method has been proposed[44] for the synthesis of substituted arenes, which is distinguished by a high regio- and stereo-specificity. It is based on the application of the reaction of orthoesters with the ethyl esters of mandelic acid and its analogues:

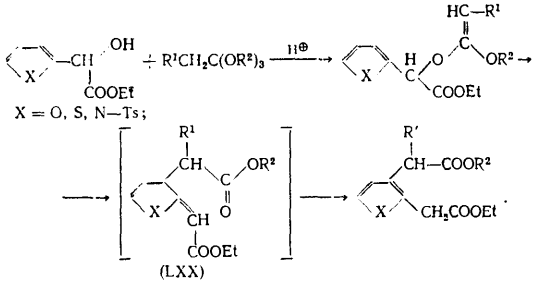



In the first stage of the synthesis, one alkoxy-group of the orthoester is substituted by the alkoxy-residue of the initial alcohol; the alcohol $R^3OH$ is split off from the product (LXIX) and this is followed by the Claisen rearrangement proper, which leads to the formation of a new carbon–carbon bond. The influence of neighbours of the hydroxy- and ethoxycarbonyl groups facilitates the intramolecular rearrangement.

The same chain of transformations is observed in the reactions of alkyl orthoesters with the esters and amides of 3-indolylglycolic acid:[44]



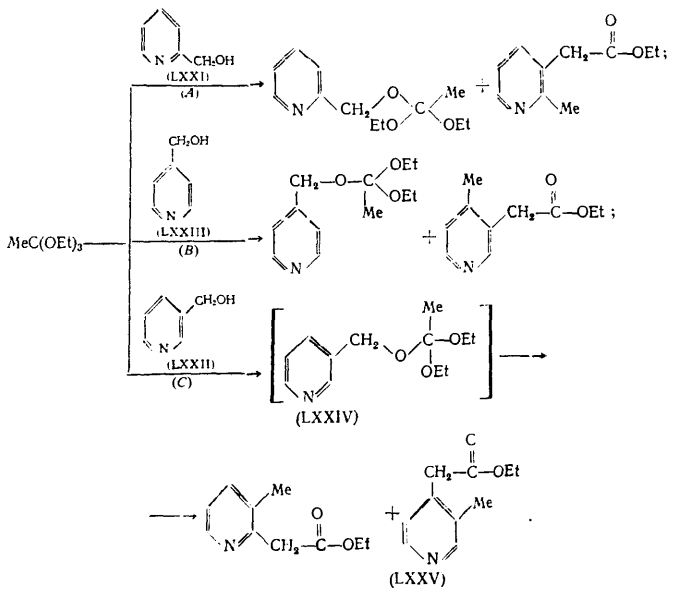
The interaction of orthoesters with other heterocyclic hydroxyesters proceeds analogously to the reaction described above,[45,46] but in this instance it is necessary to introduce an acid catalyst. 2,3-Disubstituted derivatives of furan, thiophen, and pyrrole are obtained in this way using hexanoic acid as the catalyst:[45]



The ethoxycarbonyl group stabilises the intermediate (LXX). When 3-substituted furans, thiophens, and pyrroles are used as the initial derivatives, mixtures of 2,3- and 3,4-disubstituted heterocyclic products are formed.[45]

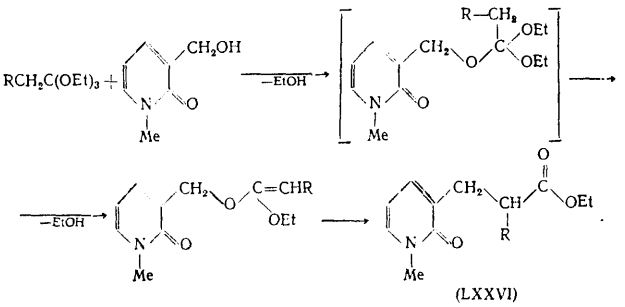
The Claisen rearrangement can also be studied for a series of hydroxymethylpyridines and hydroxymethylpyridones;[46] the authors noted that the rearrangement involving the latter proceeds in an unusual manner.

An essential condition for the smooth rearrangement in the reaction of orthoesters with the pyridine derivatives (LXXI) to (LXXIII) is an increase of temperature to 195 °C. The results of the reactions (*A*) and (*B*) of triethyl orthoacetate with 2- and 4-hydroxymethylpyridines differ from the results obtained for 3-hydroxymethylpyridine [reaction (*C*)] in which the rearranged product (LXXIV) was not isolated at all:

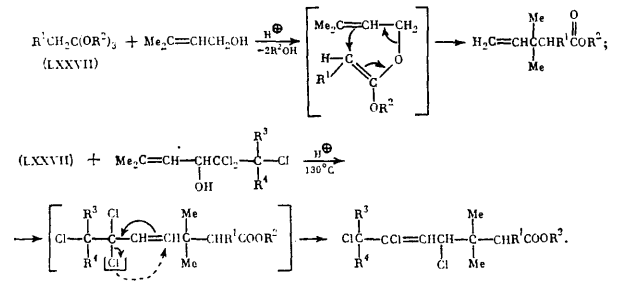


Calculation of the relative electron densities in different positions in the pyridine ring has shown that the density is a maximum in the 3-position. These data explain why the carbon–oxygen bond in compound (LXXIV) is dissociated much more readily than in the other two cases. This is why the product (LXXIV) has not been detected.

The reaction of orthoesters with 3-hydroxylmethyl-1-methyl-2-pyridine does not lead to the formation of products of type (LXXV), compounds (LXXVI) being formed instead:

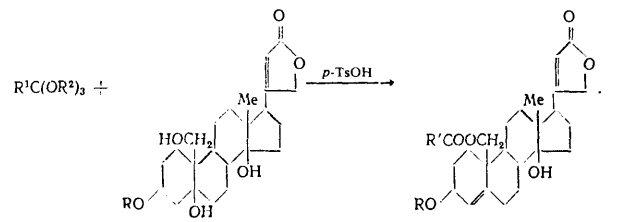


The interaction with unsaturated acyclic alcohols is used for different purposes. New methods of synthesis of unsaturated carboxylic acid esters are based on the reactions of orthoesters with allyl alcohols,[47,48] including halogenoalkyl-substituted derivatives.[49] The reaction is carried out in the presence of acid catalysts with the simultaneous removal of the lower alcohol formed as a side product, while in the case of halogeno-derivatives it is performed at elevated temperatures in a stream of nitrogen:

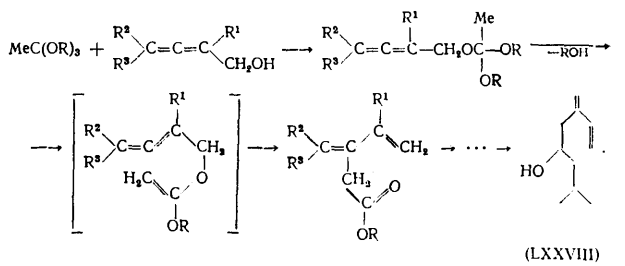


In the latter case the Claisen rearrangement is accompanied by the transfer of the chloride anion and the migration of the double bond.[49]

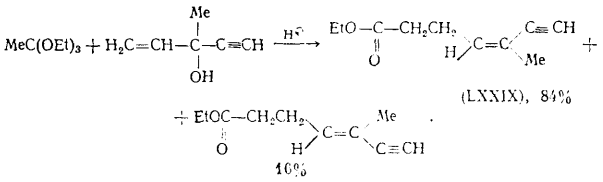
The synthesis of analogues of cardiotonic glycosides (by the conversion of cardenolides into cardadienolides) has been achieved with the aid of alkyl orthoesters:[50]



The reactions of orthoesters with alcohols of the type of allenylmethanol have been used in one of the stages of the synthesis of the terpenoids ipsenol (LXXVIII) and ipsdienol:[51]

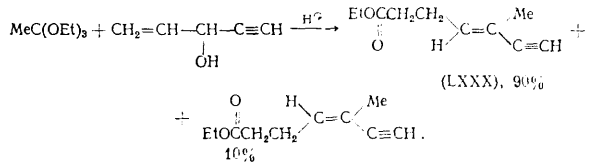


The reactions of orthoesters with vinylalkynylmethanols have been studied in detail.[52] Attention has been concentrated on the study of the structure of the product. It has been shown that the reactions of triethyl orthoacetate and tertiary allylalkynyl alcohols followed by the Claisen rearrangement yields mainly the esters (LXXIX), in which the acetylenic group occupies the *cis*-position relative to the ester side chain. The *trans*-products are formed in very small amounts, for example:



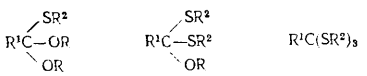
(LXXIX), 84%

The reactions of orthoesters with secondary allylalkynyl alcohols also proceed stereospecifically, although in this instance the products are mainly the *trans*-substituted compounds (LXXX):



(LXXX), 90%

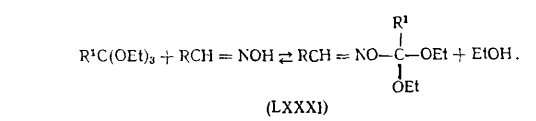
The reactions involving the exchange of the alkoxy-group of the orthoester for the alkylthio-group of a mercapto-compound are analogous to the reactions with alcohols[1,4-6] but proceed more vigorously. Thio-analogues of orthoesters the same three types as the products of the reactions with alcohols can be obtained:



By varying the conditions (by altering the temperature and the reactant ratio and by selecting the appropriate catalyst), it is possible to increase the yield of derivatives of all these types. For example, the use of aluminium chloride as the catalyst promotes the formation of mainly trithio-orthoesters.[53]

### 3. Reactions with Oximes

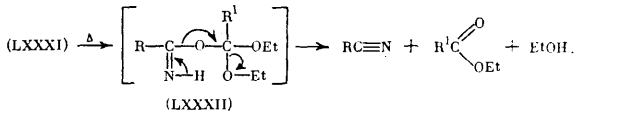
Orthoesters readily react with oximes, whereupon one alkoxy-group of the orthoester is substituted by the oxime residue formed after the abstraction of a proton:[54]



(LXXXI)

When the reactivities of the stereoisomers of oximes were compared, it was found that the *Z*-isomer reacts with the orthoester more slowly than the *E*-isomer and NMR data showed that the oxime does not isomerise under the given conditions.

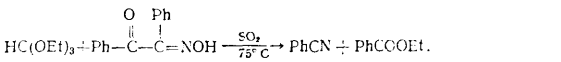
It is important to note that only in the absence of acids are the derivatives (LXXXI) relatively stable; under the conditions of acid catalysis, they undergo the "Beckmann fragmentation", which yields the corresponding nitrile, ester, and alcohol. Judging from the structure of the product (LXXXI) and the substances obtained after its fragmentation, one can postulate that the Beckmann rearrangement takes place initially and is followed by the decomposition of the product (LXXXII):



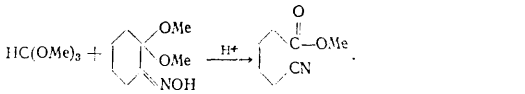
(LXXXII)

The reactions between orthoesters and oximes in liquid sulphur dioxide take place over a period of several minutes, because the solvent plays the role of the catalyst.

Thus the interaction of orthoesters with oximes constitutes an effective method of synthesis of the corresponding nitriles.[54] For example, when benzil monoxime is heated with a 10% excess of triethyl orthoformate in liquid sulphur dioxide at 75 °C, benzonitrile and ethyl benzoate can be obtained in quantitative yields:

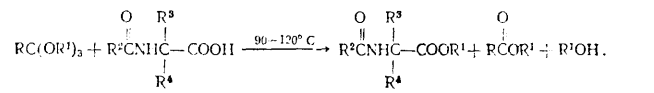


Trimethyl orthoformate and the dimethyl ketal of 2-hydroxyiminocyclohexanone react analogously in the presence of methane sulphonic acid at −10 °C to form methyl 5-cyanopentanoate:



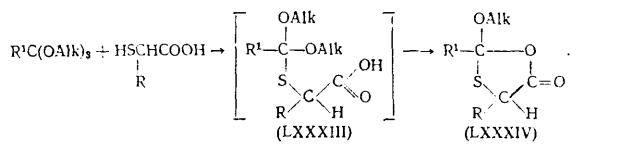
### 4. Reactions with Carboxylic Acids

The high reactivity of orthoesters makes it possible to use them for the esterification of carboxylic acids.[55] The esters of orthocarbonic and orthoacetic acids give rise to the corresponding *N*-acylaminoacid esters in quantitative yield in the absence of catalysts:[56]



The reaction is not accompanied by side processes and racemisation and proceeds smoothly even in the case of sterically hindered aminoacids.

Orthoesters react very readily with carboxylic α-mercaptoacids.[57,58] The products are 2-alkoxy-1,3-oxathiolan-5-ones (LXXXIV). It is assumed that the orthoester initially reacts with the mercapto-group and that the heterocycle (LXXXIV) is formed from the intermediate (LXXXIII) as a result of the elimination of the corresponding alcohol AlkOH:



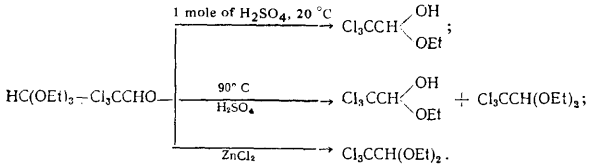
(LXXXIII) (LXXXIV)

The oxathiolanones (LXXXIV) obtained are effective reagents for the synthesis of the amides of carboxylic α-mercaptoacids.[59,60]

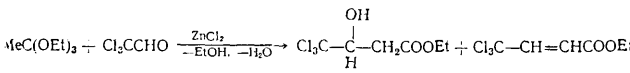
## V. INTERACTION OF ORTHOESTERS WITH CARBONYL COMPOUNDS

### 1. Reactions with Aldehydes and Ketones

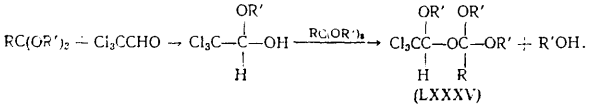
The application of orthoesters in the synthesis of acetals and ketals has been studied in fair detail. However, there is little information in the literature about the interaction of orthoesters with perhalogeno-derivatives of aldehydes and ketones.[61,62] The reaction of orthoesters with chloral is of interest.[61] In the presence of acid catalysts chloral gives rise to hemiacetals and acetals, like all other aldehydes:



In the presence of zinc chloride, ethyl orthoformate and ethyl orthocarbonate react with chloral to form only the corresponding diethyl acetal, while ethyl orthoacetate behaves differently in this reaction. Its interaction with chloral yielded a mixture of the ethyl esters of 4,4,4-trichloro-3-hydroxybutanoic and trichlorobutanoic acids:



The reaction of orthoesters with chloral takes place in an unusual manner in the absence of catalysts:



(LXXXV)

It has been found that, when weak bases (whose p$K$ does not exceed the limits 7.4–9.2) are used as the catalyst and the reaction temperature is raised to 100 °C, the yield of the product (LXXXV) rises considerably (from 18 to 60%). The mechanism of the reaction involving bases has not unfortunately been discussed by Petrov et al.[61] A product of type (LXXXV) is formed in the reaction of orthoformate with fluoral (with a higher yield).[62]

Even in the absence of catalysts, orthoformates and orthoacetates react vigorously with the hydrates of fluoral, hexafluoroacetone, and dichlorotetrafluoroacetone, forming hemiacetals and hemiketals.[62] On raising the reaction temperature to 60 °C, ethyl orthoacetate undergoes a reaction with fluoral of the type of aldol condensation, which demonstrates the relative mobility of the α-protons in the orthoacetate molecule:

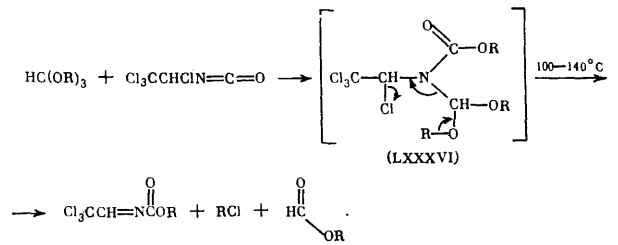


Similar products are obtained also in the reactions of alkyl orthoacetates with hexafluoroacetone and dichlorotetrafluoroacetone.

### 2. Reactions with Isocyanates

The products of the reactions of orthoesters with isocyanates vary as a function of the reactivity and structure of the isocyanate.

Being more reactive, α- and β-chloro-substituted alkyl isocyanates react with orthoesters in the absence of catalytic additives, which leads to the formation of chloro-substituted $N$-alkoxycarbonylaldimines.[63] The reaction has been followed with the aid of IR spectroscopy. The IR spectroscopic data led to the hypothesis that the intermediate (LXXXVI) is formed. The final products are an azomethine, an alkyl halide, and a formate:

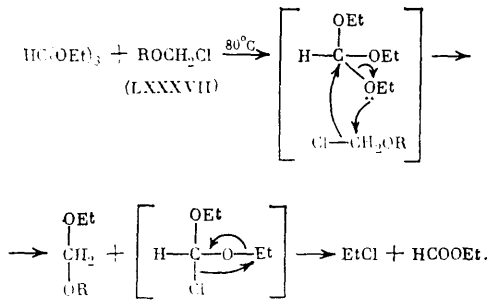


(LXXXVI)

## VI. REACTIONS OF ORTHOESTERS WITH COMPOUNDS CONTAINING AN ACTIVE HALOGEN ATOM

### 1. Reactions with Halogenoethers

One of the non-traditional methods of synthesis of mixed formals and acetals is based on the reaction of alkyl orthoesters with α-chloroethers.[64] The active halogen atom in the initial reactant (LXXXVII) is substituted by the alkoxy-group of the orthoester. The most reactive halogenoethers, for example α-chloromethyl ether, react with orthoesters at room temperature. The tentative reaction mechanism is



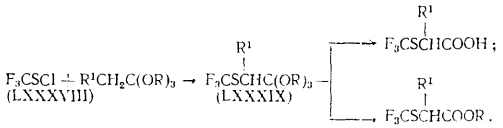
The method is simple and convenient and ensures a high yield of the required product.[64]

### 2. Reactions with Sulphenyl Chlorides

A new method for the sulphenation of orthoesters with the aid of trihalogenomethanesulphenyl chlorides has been proposed.[65] The mono- and bis-(trihalogenomethylthio)-orthoesters obtained in satisfactory yields are intermediates in the synthesis of halogenoalkylthio-derivatives of carboxylic acids.

Trifluoromethanesulphenyl chloride (LXXXVIII) is the most reactive among the proposed sulphenating agents. Its interaction with the orthoester is completed after several seconds by the formation of the monothio-derivatives (LXXXIX); the orthoester is taken in excess and the reaction is carried out

with cooling (between −10° and +10 °C):

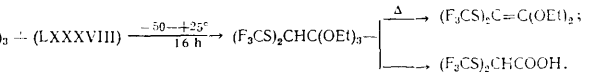


Even "inert" orthoesters such as, for example, ethyl orthoisobutyrate, react with compound (LXXXVIII), because steric factors are not decisive in this reaction:

$$(\text{LXXXVIII}) + Me_2CHC(OEt)_3 \rightarrow F_3CSCMe_2C(OEt)_3 .$$

The yield of the monosulphenated products (LXXXIX) is 75–80%. The behaviour of dichlorofluoromethanesulphenyl chloride in the reactions with orthoesters is similar to that of compound (LXXXVIII).

If the sulphenating agent is taken in excess and at the same time the reaction time and temperature are increased, only bis(trihalogenomethylthio)orthoesters are formed. They are less stable than the monothio-derivatives, so that they are converted into 2,2-dialkoxy-1,1-dialkylthioethylenes even during distillation with elimination of an alcohol molecule:



According to Mendelson et al.[65], trichloromethanesulphenyl chloride interacts with orthoesters via a radical mechanism. Orthoesters react with this compound only in the presence of a free radical initiator—azobisisobutyronitrile (XC):

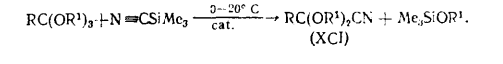
$$MeC(OR)_3 + Cl_3CSCl \xrightarrow{(XC),\ 80^\circ C} Cl_3CSCH_2C(OR)_3 .$$

The proposed reaction mechanism is

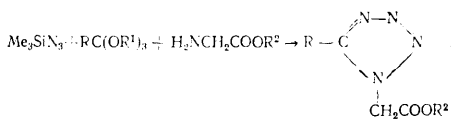
$$Cl_3CSCl \xrightarrow{(XC)} Cl_3C\dot{S} + \dot{C}l ;$$
$$\dot{C}l + CH_3C(OR)_3 \rightarrow \dot{C}H_2C(OR)_3 + HCl ;$$
$$Cl_3CSCl + \dot{C}H_2C(OR)_3 \rightarrow \dot{C}l + Cl_3CSCH_2C(OR)_3 ;$$
$$Cl_3C\dot{S} + \dot{C}H_2C(OR)_3 \rightarrow Cl_3CSCH_2C(OR)_3 .$$

## VII. INTERACTION OF ORTHOESTERS WITH ORGANOSILICON COMPOUNDS

Alkyl orthoesters and cyanotrimethylsilane are convenient reagents for the synthesis of nitriles of type (XCI).[66,67] The reaction proceeds in the presence of Lewis acids as catalysts: tin dichloride and boron trifluoride etherate:

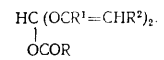


The reaction is not complicated by side processes and leads to the formation of dialkoxynitriles (XCI) in high yields. Previously acyl cyanides were used to introduce the cyano-group into the reaction with the orthoester; the reaction was as a rule accompanied by the formation of a number of side products.[68] It has been shown[69] that trimethylsilyl azide is an effective and at the same time a non-explosive reagent for the synthesis of 1-substituted tetrazole derivatives from orthoesters and aminoacid esters. The method ensures a high yield (90%) and a purity of the product not less than 95%:

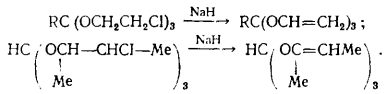


## VIII. DEHYDROHALOGENATION OF HALOGENOALKYL ORTHOESTERS

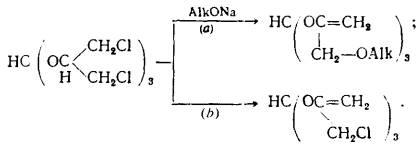
Alkenyl orthoesters,[70] compounds which are known to be highly reactive, are obtained by the dehydrohalogenation of β-chloroalkyl orthoesters. Their application in the synthesis of di(alkenyloxy)alkyl carboxylates has been described:[70]



The dehydrohalogenation of β-chloro-derivatives of orthoesters is carried out by treatment with sodium hydride or sodium butoxide:



When halogenoalkyl orthoesters are treated with solutions of alkoxides, the exchange reaction (*a*) takes place together with the elimination reaction. This side reaction can be excluded by using potassium hydroxide in an aqueous organic medium as the dehydrohalogenating agent [reaction (*b*)]:



## IX. INTERACTION OF ALKYL ORTHOESTERS WITH SULPHUR DIOXIDE

In a number of instances liquefied sulphur dioxide is used as the solvent for reactions with orthoesters. It is noteworthy that this compound is not inert with respect to orthoesters. Depending on the conditions, the products of the interaction of alkyl orthoesters with sulphur dioxide can be various.

It has been established that,[71] at low temperatures after prolonged irradiation with UV light, orthoformates and orthocarbonates give rise to the corresponding trialkoxycarbonium ions in liquid sulphur dioxide:

$$HC(OMe)_3 \rightarrow \overset{\oplus}{C}(OMe)_3 ;$$
$$HC(OEt)_3 \rightarrow \overset{\oplus}{C}(OEt)_3 ;$$
$$C(OMe)_4 \rightarrow \overset{\oplus}{C}(OMe)_3 .$$

When the temperature is raised to −20 °C, the above carbonium ions begin to decompose and are converted into dialkyl carbonates. It has been suggested that[71] the carbonium

ions are formed with direct participation of sulphur dioxide:

$$(RO)_3C{-}H \xrightarrow[h\nu]{SO_2} (RO)_3C{-}SO_2H \rightarrow \overset{\oplus}{C}(OR)_3.$$

This reaction takes place under extensive cooling conditions (−75 °C) as a consequence of the activation of the molecules by UV irradiation.

Apart from the main product, the side product (XCII) was isolated. It is formed as a result of the addition of the nucleophile ($SO_2$) to the electropositive carbon atom of the alkoxy-group of the orthoester:

$$(MeO)_2CHOMe \xrightarrow{SO_2} \underset{(XCII)}{(MeO)_2CHOCH_2SO_2H}.$$

If the mixture of liquefied sulphur dioxide with the alkyl orthoester is maintained in a sealed tube at room temperature, the reaction products are dialkyl sulphites and esters:[72]

$$RC(OR^1)_3 + SO_2 \xrightarrow[24\ h]{20^\circ C} O{=}S\begin{matrix}OR^1\\OR^1\end{matrix} + RCOOR^1.$$

Orthoformate, which is relatively passive in sulphur dioxide in the absence of irradiation, is an exception. Only on heating with a large excess of $SO_2$ does it react slowly, forming diethyl carbonate in addition to ethyl formate and diethyl sulphite.

It has been shown with the aid of $^1H$ NMR [72] that the addition of even catalytic amounts of $SO_2$ to mixtures of orthoesters entails the immediate exchange of the alkoxy-groups as a consequence of the appearance of dialkoxyalkylcarbonium ions. The proposed mechanism of the reaction with $SO_2$ is as follows:

$$RC(OEt)_3 + SO_2 \underset{}{\overset{(A)}{\rightleftharpoons}} \underset{(XCIII)}{R{-}\overset{\oplus}{C}(OEt)_2{-}O{-}SO_2^{\ominus}Et};$$

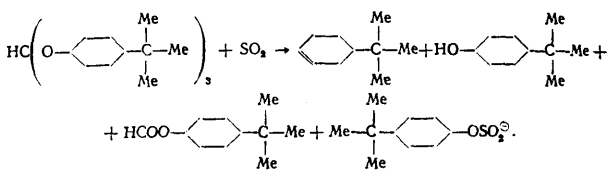
$$(XCIII) \overset{(B)}{\rightleftharpoons} \overset{\oplus}{R}C(OEt)_2 + EtOSO_2^{\ominus};$$

$$R{-}\overset{\oplus}{C}(OEt)_2 + EtOSO_2^{\ominus} \xrightarrow{(C)} RCOOEt + (EtO)_2S{=}O;$$

$$(XCIII) + EtOSO_2^{\ominus} \xrightarrow{(D)} RCOOEt + EtOSO_2^{\ominus} + (EtO)_2S{=}O.$$

The intermediate (XCIII) is apparently formed via the coordinate bond between the sulphur atom in sulphur dioxide and the free electron pair of the oxygen atom in the alkoxy-group of the orthoester (*A*). It decomposes subsequently at the C–O bond (*B*). Both these reactions are reversible. It has been suggested that the main reaction products are obtained as a result of the attack by the alkyl sulphite anion on the dialkoxycarbonium ion (*C*) or on the intermediate (XCIII) (*D*).

The validity of the proposed mechanism has been confirmed by the behaviour of secondary trialkoxymethanes in reactions with $SO_2$ under the same conditions. The substitution by the resulting secondary alkyl sulphite anion at a secondary carbon atom of the carbonium ion (XCIV) is sterically hindered and for this reason the corresponding olefin, alkanol, secondary alkyl formate, and alkylsulphurous acid are formed. For example:[72]



Thus, in contrast to the photochemical reaction, the interaction of orthoester molecules with $SO_2$ in the absence of a supply of energy from outside leads to the formation of dialkoxycarbonium ions which are less stable than trialkoxycarbonium ions.

## X. BROMINATION OF ORTHOESTERS

The behaviour of dimethoxycarbenium bromides in liquid sulphur dioxide has been investigated.[73] The orthoesters were brominated at temperatures between −60° and −80 °C. Orthoesters react with bromine via an ionic mechanism and the reaction was followed with the aid of NMR. It is a typical nucleophilic substitution reaction. The $Br^{\oplus}$ ion abstracts the alkoxide anion from the orthoester molecule and $Br^{\ominus}$ promotes the stabilisation of the dialkoxyalkylcarbonium ion formed:

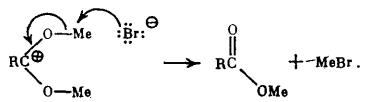
$$RC(OR^1)_3 + Br_2 \rightarrow RC\begin{matrix}OR^1\\OR^1\end{matrix}{}^{\oplus}\ Br^{\ominus} + BrOR^1.$$

It has been shown that, when the orthoesters are brominated in the presence of orthocarbonate, the more stable trialkoxycarbonium ions are formed. This takes place via the irreversible migration of the methoxy-group from the orthocarbonate to the dialkoxycarbonium ion:

$$RC\begin{matrix}OMe\\OMe\end{matrix}{}^{\oplus}\ Br^{\ominus} + Br_2 + C(OMe)_4 \xrightarrow[SO_2]{-80^\circ C} RC(OMe)_3 + MeO{-}\overset{\oplus}{C}(OMe)_2Br^{\ominus}.$$

The role of the solvent was not discussed in the above communication.

Dimethoxycarbenium bromides are stable only at temperatures below −50 °C, decomposing at higher temperatures in accordance with the following scheme:



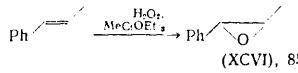
## XI. ORTHOESTERS IN TRANSFER OXIDATION REACTIONS

It has been found[74,75] that, in the presence of orthoesters, hydrogen peroxide can be conveneintly used for the mild oxidation of olefins to the corresponding epoxy-derivative. It has been suggested that orthoesters interact with hydrogen peroxide to form the intermediate (XCV) (these are relatively stable as a result of hydrogen bonding), which serve as agents which transfer and generate atomic oxygen:

$$C(OEt)_4 + H_2O_2 \xrightarrow{-EtOH} \underset{(XCV)}{\left[\begin{matrix}EtO\cdots H\\ \diagdown\\ EtO{-}C{-}O\\ |\\ OEt\end{matrix}\right]} \xrightarrow{-EtOH} [O] + (EtO)_2CO.$$

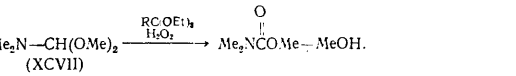
The ethyl esters of formic, acetic, orthobenzoic, and carbonic acids have been tried together with hydrogen peroxide as transfer oxidising agents. Regardless of the structure of the olefin oxidised, the best results were obtained in the first place using ethyl orthocarbonate and then ethyl orthoacetate. This method makes it possible to obtain epoxy-derivatives which are otherwise difficult to

synthesise, for example, compound (XCVI), in a higher yield:



(XCVI), 85%

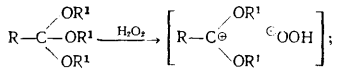
Peroxides such as 9,10-endoperoxy-9,10-diphenylanthracene, can be obtained by the same procedure. Oxidation of the amidoacetals (XCVII) by this method leads to the isolation of the corresponding carbamates:



(XCVII)

The reaction mechanism has not been specially investigated. The hypothetical structure of the intermediate (XCV) has not been confirmed by physicochemical research techniques. We believe the hypothesis that the active oxidising agent may be an ionic complex of type (XCVIII) to be acceptable.

Like other weak acids, hydrogen peroxide added to orthoesters is capable of producing dialkoxycarbonium ions, which are stabilised by combining with the anion $HOO^{\ominus}$:



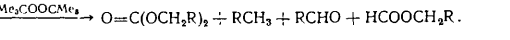
(XCVIII)

R=Me (a), $OR^1$ (b), Ph (c);
$R^1$=Et.

Since the complexes (XCVIIIb) are more stable than the complexes (XCVIIIa) while complexes of type (XCVIIIc) are relatively stable but sterically hindered compared with (XCVIIIa), the reason why orthocarbonate is preferable to other orthoesters becomes understandable.

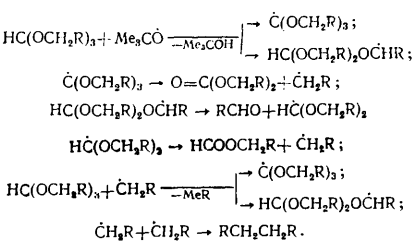
## XII. FREE-RADICAL REACTIONS OF ORTHOESTERS

Two investigations have been made of the behaviour of trialkoxymethanes in reactions with free radicals at elevated temperatures (120–150 °C).[76,77] It has been shown by EPR that alkyl orthoformates react with free radicals to form tri- and mono-alkoxyalkyl radicals, whose fragmentation leads to the formation of the corresponding carbonates and formates. The radical reactions were initiated by t-butoxy-radicals:



Conclusions concerning the reactivity of orthoformates in reactions of the above type compared with linear and cyclic acetals were reached on the basis of kinetic data.

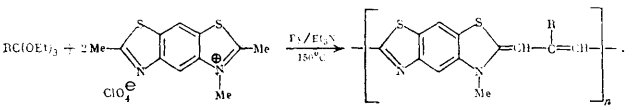
The mechanism of the homolytic liquid-phase reactions of alkyl orthoformates can be demonstrated in relation to triethoxymethane:



It was found that radical chain reactions involving orthoesters can be observed also at much lower temperatures (60 °C) when dicyclohexyl peroxycarbonate is used as the free radical initiator.[78] The chain of radical reactions is analogous to that described above and the main products are the same as under high-temperature conditions.

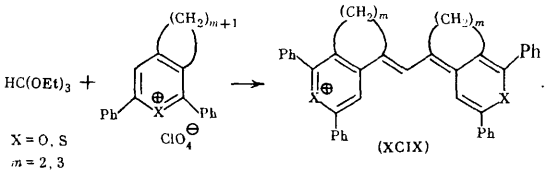
## XIII. SOME APPLICATIONS OF ORTHOESTERS

Orthoesters have been known for a long time as irreplaceable reagents in the synthesis of dyes.[4] Progress in the field of cyanine dyes has continued successfully.[79] A new method of synthesis of polymeric cyanines based on orthoesters and 2,3,6-trimethylthiazolo[4,5-*f*]benzothiazolium perchlorate in the presence of weak organic bases has been proposed:[80]



The reaction conditions make it possible to achieve a high degree of condensation, which is favourably reflected in the quality of the dyes obtained.

Pyrylocarbocyanines (XCIX),[81] which are geometrical isomers of the pyrylo-2-cyanines described previously,[82] have been obtained[81] by the reaction of diethyl orthoformate salts of the diphenyl-substituted derivatives of cyclopenta-[c]pyrylium and also its thio-analogue and 5,6,7,8-tetrahydrobenzo-3,4-pyrylium:



(XCIX)

It has been shown[81,82] that the introduction of bridging ethylene and trimethylethylene groups not only stabilises the dyes obtained but also deepens their colour.

Derivatives of isoxazolopyrimidine, which exhibit a high selective herbicidal activity before and after germination, have been obtained by a series of reactions from aliphatic alkyl orthoesters and malononitrile.[83] Propyl orthocarbonate and propyl orthobenzoate proved to be highly effective additives leading to the manifestation of synergism by certain insecticides.[84]

The possibility of using orthoesters, apart from aldehydes and epoxides, in the catalytic carbonylation reactions in the presence of carboxylic acid amides in order to obtain N-acyl-α-aminoacids has been discovered.[85]

Orthoesters have found the widest applications as components of active and stereospecific catalysts in the polymerisation of propene[86–89] and ethylene,[90] while aminoalkyl orthoesters are most widely used in the synthesis of polyurethanes[41–43] and polyisocyanates.[43]

It has been found[91] that orthoesters are essential components in the synthesis of special elastic cementing materials.

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# Methods of Synthesis of Arylphosphonic and Arylphosphonothioic Acids and Their Derivatives

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A systematic account is given of data on the synthesis of arylphosphonic and arylphosphonothioic acids and their derivatives by the addition of oxygen or sulphur to arylphosphonous acids, their esters, amides, and dihalides, by treating phosphoryl chloride, dialkyl phosphorochloridates, and phosphorodiamidic chlorides with aryl-substituted organometallic compounds, by the reaction of benzene and its derivatives containing various substituents in the ring with phosphorus pentoxide, phosphorus sulphide halides, phosphorus sulphides, and esters of phosphorous and phosphorothious acids, and by other less familiar methods. The methods of synthesis of aryldihalogenophosphines, which are important intermediates in the synthesis of arylphosphonic acids and their derivatives, are described.
The bibliography includes 355 references.

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## I. INTRODUCTION

By virtue of the wide variety of their properties due to the presence of two reaction centres, namely the aromatic ring and the phosphono-group, and also as a consequence of the various aspects of their possible practical applications which have been discovered, aryl phosphonic acids and their derivatives have been the subject of numerous investigations. At present there exist extensive data on this question in both Soviet and foreign literature, but there have been no surveys with the exception of two published in 1957–1958 in which the data accumulated were only partly utilised.[1,2] This review deals with data on the methods of synthesis of arylphosphonic and arylphosphonothioic acids and their derivatives which have been published up to the middle of 1984.

## II. METHODS OF SYNTHESIS OF ARYLPHOSPHONIC ACIDS AND THEIR DERIVATIVES

Arylphosphonic acids and their derivatives are obtained by various procedures which can be divided into two groups. The first group includes methods based on the oxidation of arylphosphonous acids and their derivatives and the second includes methods which lead to the formation of a phosphorus–carbon bond.

### 1. Oxidation of Arylphosphonous Acids and Their Derivatives

Apart from the oxidation of arylphosphonous acids and their salts, esters, amides, and chlorides, this Section also includes the reactions of α-chlorocarbonyl compounds with arylphosphonites. Arylphosphonous acids and their salts, esters, and amides are oxidised by oxygen,[3–5] hydrogen peroxide,[3,6] manganese dioxide,[7] calomel,[8] nitric acid,[9,10] and chlorine[11,12] to phosphonic acids and their derivatives. The reaction of the esters and ester imides of arylphosphonous acids with chloral leads to derivatives of arylphosphonic acids containing the dichlorovinyl group in the ester moiety in yields up to 79.5%:[13–15]

$$R^1C_6H_4P(OR^2)(XR^2) + OCHCCl_3 \rightarrow R^1C_6H_4(O)P(OCH{=}CCl_2)XR^2\ ;$$
$$R^1{=}H, Cl;\ R^2 = C_1\text{–}C_4\ \text{alkyl},\ (CH_2CH_2O)_2CH_3;\ X{=}O, NCH_3\ .$$

Various derivatives of chloroacetoacetic acid react similarly with arylphosphonites:[16]

$$R^1C_6H_4P(OR^2)_2 + R^2C(O)CHClCOOC_2H_5 \rightarrow$$
$$\rightarrow R^1C_6H_4(O)P(OCR^2{=}CHCOOC_2H_5)OR^2\ ;$$
$$R^1{=}H, CH_3, C_2H_5, N(CH_3)_2, N(CH_3)C_6H_5, NO_2;\ R^2 = C_1\text{–}C_4\ \text{alkyl}.$$

Aryldihalogenophosphines are oxidised by oxygen,[17–19] chlorine or bromine in t-butyl alcohol,[20] chlorine with subsequent treatment of the reaction mixture with sulphur dioxide,[21–26] acetals[27] or ketones,[28] chlorine in the presence of phosphorus pentoxide,[29–31] and sulphuryl chloride[29,32–35] with formation of arylphosphonic acid dichlorides in yields of 70–98%. Aryl dihalogenophosphines in the form of aluminium chloride complexes can be used in the oxidation reaction. In certain cases the oxidised complex is esterified with an excess of alcohol and then subjected to acid hydrolysis.[36–42]

The dichloride of phenylphosphonic acid is obtained also by the reaction of the thioanhydride of phenylphosphonothious acid with sulphuryl chloride[43] or by the successive treatment of phenylphosphonothioic dichloride (and also its mixture with phenylphosphonic acid) with chlorine and sulphur dioxide.[44,45]

### 2. Methods of Synthesis of Aryldihalogenophosphines

All the derivatives of arylphosphorous acids enumerated in the previous Section are usually obtained from aryldihalogenophosphines,[3] the main methods of synthesis of which are considered in this Section.

#### (a) Arylation of Phosphorus Halides by Aromatic Hydrocarbons

At a temperature above 550 °C benzene interacts with phosphorus pentachloride, the degree of conversion of which into dichlorophenylphosphine for a phosphorus pentachloride : benzene molar ratio of 1 : 14 reaches 8%.[19] Dichlorophenyl- and dichlorotolyl-phosphines are formed when benzene or toluene interacts with phosphorus trichloride at 500–600 °C.[46–52] The yield of dichlorophosphines reaches 70–99% when the reaction is carried out in the presence of

catalysts: oxygen,[53] alkyl halides,[54] phosgene,[55] or zeolites.[56–58] When anhydrous aluminium chloride is used as the catalyst, the phosphorylation temperature is reduced to 60–80 °C. Aryl dichlorophosphines with a small admixture of diarylchlorophosphines are obtained in the form of complexes with aluminium chloride:[36,59–61]

$$ArH + PCl_3 + AlCl_3 \rightarrow ArPCl_2 \cdot AlCl_3 + HCl \ .$$

Equimolar ratios of the aromatic hydrocarbon and aluminium chloride are usually employed with a not less than a threefold excess of phosphorus trichloride, because otherwise the amount of the diarylchlorophosphine impurity increases sharply. The reaction time varies from 1 to 8 h. After more prolonged refluxing (36 and more hours), the content of diarylchlorophosphines rises to 30% and more.[36]

Aryldichlorophosphines are isolated from the complex by treatment with phosphoryl chloride,[21,62–64] pyridine,[65,66] phosphoric acid, tri(2-chloroethyl)phosphate,[67–69] ethers and esters, ketones,[70] or the calculated amount of water.[64,71] After the decomposition of the complex, the aryldichlorophosphine is extracted with benzene,[67] petroleum ether,[9,64,72] or phosphorus trichloride[63,73] and is isolated by distillation.

The method is convenient in laboratory practice and has been tested on an experimental apparatus in the synthesis of dichlorophenyl- or dichloro-4-tolyl-phosphines.[74] It makes it possible to obtain aryldichlorophosphines containing one or several substituents in the ring. Thus, when phosphorus trichloride interacts with benzene, toluene, ethylbenzene, xylene, 1,2-diphenylethane, and diphenylmethane, dichlorophenyl-,[9,10,21,23,36,63–70,74–79] dichlorotolyl-,[21,40,73,74,80] dichloroethylphenyl-,[21,40,62,81,82] dichloroxylyl-,[77,78,80,81,83,84] dichloro(4-phenylethylphenyl)-,[80] and 4-benzylphenyldichloro-phosphines[80,85,86] are formed respectively. When biphenyl and bidenzofuran are used, the corresponding mono- and bis-dichlorophosphines are formed depending on the reactant ratio.[80,86–88]

When alkylbenzenes ($RC_6H_5$) are phosphorylated, the yield of aryldichlorophosphines ($RC_6H_4PCl_2$) diminishes with increase of the length of the alkyl group from 60–89% for $R = CH_3$ or $C_2H_5$ to 33–39% for $R = C_4H_9$.[21] The phosphorylation of monoalkylbenzenes always leads to a mixture of isomeric dichlorophosphines. For example, dichlorotolylphosphine is a mixture of the 4-, 3-, and 2-isomers in proportions of 63 : 27 : 10 and dichloroethylphenylphosphine is a mixture of the 4- and 3-isomers.[40,81] The methyl groups in the dichlorophosphine prepared from *p*-xylene are in the 2- and 5-positions,[81] while in the case of *o*-xylene the product is dichloro-3,4-dimethylphenylphosphine.[84] When trifluoromethanesulphonic acid is used instead of aluminium trichloride, the yield of dichloro-3,4-dimethylphenylphosphine is 33%.[89] The phosphorylation of pseudocumene and mesitylene leads to the formation of the corresponding dichlorophosphines in 45% yield,[90,91] while phosphorylation of the symmetrical tri-t-butylbenzene gives rise to the corresponding phosphines in 71% yield.[92] Alkylbenzenes containing a silicon atom in the side chain are phosphorylated to aryldichlorophosphines, the yield of the mixture of 4- and 2-isomers amounting to 32–52%:[93,94]

$$Cl_n(CH_3)_{3-n}Si(CH_2)_m C_6H_5 + PCl_3 \xrightarrow{AlCl_3} Cl_n(CH_3)_{3-n}Si(CH_2)_m C_6H_4PCl_2;$$
$$n, m = 1-3 \ .$$

Aryl halides are also phosphorylated: on being refluxed with phosphorus trichloride and aluminium chloride, fluorobenzene affords dichloro-4-fluorophenylphosphine in 45 to 65% yield,[24,95–97] while chlorobenzene gives rise to a mixture of the isomeric chlorophenyldichlorophosphines in yields up to 80%,[36,63,73,81,98–100] the 4-isomer predominating.[34,97,101] When bromobenzene is phosphorylated, the yield of 4-bromophenyldichlorophosphine varied from 14 to 51%, depending on the reaction conditions,[23,72,73,97] while the yield of the 2-bromoisomer is 41.5%.[32] 3-Chloro-4-tolyldichlorophosphine has been obtained from 2-chlorotoluene in 10–15% yield.[22]

After 1,2- and 1,4-dichlorobenzenes have been refluxed for a long time with phosphorus trichloride and aluminium chloride, the products are respectively 3,4- and 2,5-dichlorophenyldichlorophosphines which were identified in the form of arylphosphonic acids; the yield of products is then appreciably lower than in the case of chlorobenzene, while trichlorobenzenes do not undergo the phosphorylation reaction at all.[36]

The polyfluorobenzenes $C_6HF_4R$ with $R = NO_2$ and $CH_2SO_2$ do not undergo the phosphorylation reaction, the phosphorylation of derivatives with $R = OCH_3$ and $SCH_3$ is accompanied by the dissolution of the ester linkage, while compounds with R = H, F, or $CF_3$ produce dichlorophosphines in yields of 37–53%.[102]

The alkyl esters or thioethers of monohydric and dihydric phenols are phosphorylated by phosphorus trichloride in the presence of aluminium, iron, and zinc chlorides with formation of 4-alkoxyphenyldichlorophosphines in yields not exceeding 39%,[23,72,80,103–106] while in the presence of stannic chloride the yield is 26–91%:[107,108]

$$R^1R^2R^3C_6H_3 + PCl_3 \rightarrow R^1R^2R^3C_6H_2PCl_2$$
$$R^1 = H, C_1\text{–}C_4 \text{ alkyl}; \ R^2 = OR^1, SCH_3; \ R^3 = H, CH_3, OCH_3 \ .$$

When the dimethyl ether of resorcinal was phosphorylated in the presence of iron(III) chloride, dichloro-2,4-dimethoxyphenylphosphine was obtained in 27% yield,[109] when zinc chloride in a proportion not more than 0.06 mol per mole of the ether was used, the yield of the aryldichlorophosphine was 69%, while in the presence of an equimolar amount of zinc chloride only tris(2,4-dimethoxyphenyl)phosphine was formed in 14% yield.[35,103]

Diphenyl ether reacts with phosphorus trichloride and aluminium chloride, taken in molar proportions of 1 : 1 : 0.15, and gives rise to dichloro-4-phenoxyphenylphosphine in 13.7% yield.[110]

When 2,3-benzo-1,4-dioxan is heated with phosphorus trichloride and a catalytic amount of zinc chloride, the aromatic ring is phosphorylated in the *meta*-position, the yield of the corresponding dichlorophosphine being 50%.[111]

The phosphorylation of *NN*-dialkylanilines with phosphorus trichloride takes place in the absence of a catalyst, the yield of 4-*NN*-dialkylaminophenyldichlorophosphines amounting to 60–97%.[23,112,113] The presence of aluminium chloride reduces the yield to 36%.[8,114,115]

Aryldibromophosphines are obtained by heating aryldichlorophosphines with phosphorus tribromide or with gaseous hydrogen bromide.[97]

Dichlorophenylphosphine is obtained by heating a mixture of chlorodiphenyl- or triphenylphosphine with phosphorus trichloride to 350 °C.[116,117]

### (b) Arylation of Phosphorus Trihalides by Organometallic Compounds

Various aryldichlorophosphines have been synthesised by this method from diarylmercury;[3,8,48,80,118] for example, dichloro-2-tolylphosphine has been obtained in 78% yield:

$$Hg(C_6H_4R)_2 + 2PCl_3 \xrightarrow{130\text{–}230^\circ} 2RC_6H_4PCl_2 + HgCl_2 \ ;$$
$$R = H, Cl, CH_3, OCH_3, N(CH_3)_2 \ .$$

Dichlorophenyl-, dichloro-2-tolyl-, dichloro-4-tolyl-, and dichloro-4-ethylphenyl-phosphines have been obtained by heating phosphorus trichloride with the corresponding aryl–

zinc bromide (yields up to 32%) and 4-bromophenyldichlorophosphine has been obtained in a yield of 8%.[119,120] Dichloro-4-trifluoromethylphenylphosphine has been synthesised analogously.[25] When tetraphenyl-lead or tetraphenyl–tin is heated for a long time (180 h) with phosphorus trihalide, the yield of the dihalogenophenylphosphines reaches 93%,[121,122] while in the case where triphenyl–antimony and bismuth are used the yield is much lower.[123,124]

Aryldichlorophosphines, aminoarylchlorophosphines, and arylphosphonous acid amides have been obtained in yields of 32–85% by the reaction of arylmagnesium bromides with phosphorus trichloride.[102,125–127] On treatment with hydrogen chloride, the amides of arylphosphorous acids are readily converted into aryldichlorophosphines:[128]

$$(R^1_2N)_n PCl_{3-n} + ArMgBr \rightarrow (R^1_2N)_2 P(Ar) Cl_{2-n} \xrightarrow{HCl} ArPCl_2 ;$$

$R^1 = CH_3, C_2H_5$; $Ar = 2\text{-}BrC_6H_4CH_2C_6H_5$, 2-, 3- or 4-$FC_6H_4$, 4-$R^2C_6F_4$; $R^2 = H, F, Cl, CF_3, OCH_3$; $n = 0-2$ .

*o*-Phenylenebis(tetramethyldiaminophosphine) has been obtained in 84% yield by the reaction of (tetramethyldiamino)-2-lithiophenylphosphine with chloro(tetramethyldiamino)phosphine; on treatment with hydrogen chloride, the product is converted into *o*-phenylenebis(dichlorophosphine).[129]

Arylchlorosilanes are also used in the synthesis of dichlorophosphines. The reaction takes place only in the presence of aluminium chloride, which cleaves the silicon–carbon bond under mild conditions with formation of the corresponding organoaluminium compounds. The latter react with phosphorus trichloride and afford aryldichlorophosphines in yields of 77–85%:[130,131,132]

$$(R_nC_6H_{5-n})_mSiCl_{4-m} + mAlCl_3 + mPCl_3 \rightarrow mR_nC_6H_{5-n}PCl_2 \cdot AlCl_3 ;$$

$R = H, Cl, Br, C_1$–$C_4$ alkyl; $n = 0-5$; $m = 1-4$ .

### (c) Arylation of White Phosphorus by Aryl Halides

Aryl halides arylate white phosphorus at 250–450 °C in the presence of catalytic amounts of Lewis acids,[133–135] metal powders (Cu, Ag, and Zn),[136,137] or in the absence of a catalyst[138–140] with formation of a mixture of aryldihalogeno- and diarylhalogenophosphines, with the former predominating:

$$3R_nC_6H_{5-n}Hal + {}^1/_2P_4 \rightarrow R_nC_6H_{5-n}PHal_2 + (R_nC_6H_{5-n})_2PHal ;$$

$R = H, Cl, CH_3$; $Hal = Cl, Br$; $n = 1, 2$ .

When the reaction is carried out in phosphorus trihalide, the yield of aryldihalogenophosphines increases greatly, particularly in the presence of catalysts—sulphur, iodine, and halogeno-compounds. Thus dichlorophenylphosphine is obtained in 90% yield,[141–143] dibromo-2-tolylphosphine in 50.21% yield, and dichloro-4-fluorophenylphosphine in 73% yield.[144] Dichloro-2,4,5-trichlorophenylphosphine has been isolated in the form of a phosphonous acid in 57% yield.[145] The interaction of 1,4-dichlorobenzene with white phosphorus and $PCl_3$ leads to a mixture of 4-chlorophenyldichlorophosphine (I) and 1,4-bis(dichlorophosphino)benzene (II):

$$1,4\text{-}Cl_2C_6H_4 + {}^1/_2P_4 + 2PCl_3 \xrightarrow{I_2} \underset{(I)}{4\text{-}ClC_6H_4PCl_2} + \underset{(II)}{1,4\text{-}(Cl_2P)_2C_6H_4} .$$

The main reaction products are compound (I) at 290–300 °C and compound (II), in 38.4% yield, at 340 °C. Compound (I) is also converted into compound (II) on heating with white phosphorus and phosphorus dichloride, the yield being 24.7%.[146,147]

### (d) Other Methods

Aryldichlorophosphines are obtained when complexes synthesised from arenediazonium fluoroborates and phosphorus trichloride are reduced with magnesium or aluminium:[148–155]

$$RC_6H_4\overset{+}{N}_2BF_4^- \xrightarrow{PCl_3} RC_6H_4\overset{+}{P}Cl_3BF_4^- \xrightarrow{M} RC_6H_4PCl_2 ;$$

R=4-$CH_3$, 2-$C_6H_5CH_2$, 2-, 3- or 4-Cl, 3-Br, 2-$CH_3O$, 2-(4-$ClC_6H_4S$), 3- or 4-$COOC_2H_5$, 3- or 4-CN; M=Mg, Al .

The reaction is exothermic, but can be readily controlled.

Arylhydrazines and their hydrochlorides give rise to aryldichlorophosphines in 45–65% yield on refluxing with phosphorus pentachloride in benzene:[156]

$$4\text{-}RC_6H_4NHNH_2 + PCl_5 \rightarrow 4\text{-}RC_6H_4PCl_2 + N_2 + 3HCl ;$$

R=$CH_3$, Cl, Br .

Dihalogenophenylphosphines are formed in 8.5–11.5% yields when a mixture of iodobenzene, phosphorus trihalide, and powdered silver is irradiated with UV light.[157]

Thus aryldichlorophosphines are usually obtained by the Friedel–Crafts reaction, which has in fact been more thoroughly investigated than other methods. The reaction is simple to carry out, the initial rectants are readily available, and the dichlorophosphines are obtained in satisfactory yields. Significant disadvantages of the method are the formation of a mixture of the 2-, 3-, and 4-isomers of aryldichlorophosphines, which are difficult to separate, a large amount of industrial waste,† and a limited selection of substituents in the aromatic ring.

## 3. Arylation of Phosphorus Trihalides by Arenediazonium Fluoroborates

A large number of different arylphosphonic acids have been synthesised by this method, although the first attempts to employ arenediazonium salts for the synthesis of arylphosphonic acids were unsuccessful.[23,110,158,159] Later arylphosphonic acids were synthesised by the reactions of fluoroborates with phosphorus trichloride in the presence of powdered copper bronze or univalent copper halides:

$$Ar\overset{+}{N}_2BF_4^- + PCl_3 \xrightarrow{Cu \text{ or } Cu_2Cl_2} Ar\overset{+}{P}Cl_3BF_4^- \xrightarrow{H_2O} ArPO_3H_2 .$$

The reaction is carried out in an anhydrous organic solvent, mainly ethyl and isopropyl acetate or dioxan, at room temperature of 50–60 °C. The reactants are taken in equimolar proportions. Phosphorus tribromide is rarely used.[160–164] Apart from arenediazonium fluoroborates, the diazonium chlorozincate and fluorosilicate salts are used. It has been noted that diazonium fluorosilicates are more stable and more convenient to handle.[164] The required compounds are isolated from concentrated aqueous solutions in the form of monosodium (monopotassium) salts of the free acids and are purified by recrystallisation, usually from 6 *N* HCl. The yields of arylphosphonic acids normally vary in the range 10–50% and rarely exceed 70%. Diarylphosphinic acids are formed as side products in yields up to 15%.

Phenylphosphonic acid is formed from benzenediazonium fluoroborate and phosphorus trichloride in 17% yield.[161] 3- and 4-Tolylphosphonic acids have been prepared in yields of 69.8 and 60% respectively[165] and all the isomers of ethylphenylphosphonic acid have been obtained in yields of 11–18%.[166] 4-(β-Bromoethyl)phenylphosphonic and

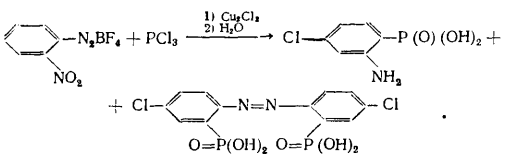
† Between 2.2 and 2.5 kg of solid waste and resins are obtained per kilogram of aryldichlorophosphine.[74]

4-(t-butyl)phenylphosphonic acids have been synthesised in yields of 36%[167] and 55%[39] respectively, while 2- and 4-biphenylylphosphonic acids have been obtained in yields of 9 and 40%.[168] (2,5-Diphenyl)phenylphosphonic acid is formed in 17% yield.[169]

Almost all the possible isomeric monohalogenophenylphosphonic acids, other than 3-bromo- and 4-iodo-substituted derivatives, have been synthesised in yields of 20–60%. They have been identified in a free state, with the exception of the 4-fluoro-derivative, which has been isolated in the form of the 4-toluidine salt. Iodobenzenediazonium salts react with phosphorus halides with greater difficulty and the yields of iodophenylphosphonic acids do not exceed 22%.[161,163,164,170–174]

When benzene-1,3- and benzene-1,4-disdiazonium fluoroborates are treated with phosphorus trichloride, only one diazo-group is phosphorylated, while the second is substituted by chlorine and partly by fluorine.[175] Di- and trihalogenobenzenediazonium fluoroborates react with phosphorus trichloride and tribromide under the same conditions to form di- and tri-halogenophenylphosphonic acids in yields up to 32%.[163,173] The isomeric 2-chloro-5-methyl-, 3-chloro-4-methyl-, and 4-chloro-3-methyl-phosphonic acids have also been obtained by this method in yields of 36, 50, and 15% respectively.[162,176]

3(4)-Nitrophenyl- and 4(5)-nitro-2(3)-tolyl-phosphonic acids are obtained by the diazo-method in yields of 37 to 55%.[161,164,174,177] 2-Nitrophenyl- and dinitrophenyl-phosphonic acids could not be obtained by this method.[161,170] The interaction of 2-nitrobenzenediazonium fluoroborate with phosphorus trichloride is accompanied not only by the substitution of the diazo-group by the dichlorophosphonyl group but also by the reduction of the nitro-group to the amino-group and by the chlorination of the aromatic ring. 2-Amino-4-chlorophenylphosphonic acid and 4,4′-dichloro-2,2′-diphosphonoazobenzene were isolated in low yields from the reaction mixture:[178]



The catalyst is used in an equivalent amount and the $ArN_2BF_4$ : $PCl_3$ ratio is 1 : 3.5. In the presence of a smaller excess of the phosphorus halide, the yield of the arylphosphonic acid is appreciably reduced. Chloroaminophenylphosphonic acid is isolated from its complex with a copper salt on treatment with hydrochloric acid in a yield up to 15%.[179–181] The phosphorylation of monohalogeno-derivatives of 2-nitrobenzenediazonium fluoroborates proceeds without the halogenation of the aromatic ring but with reduction of the nitro-group regardless of the position of the halogen atom.[182] The use of reductants, for example, of powdered iron in hydrochloric acid, makes it possible to raise the yield of 2-amino-4-halogenophenylphosphonic acids to 33%.[182] 2-Hydroxyphenylphosphonic acid cannot be synthesised by this method; only the products of its coupling with 4-nitrobenzenediazonium chloride were isolated from the reaction mixture in a small amount.[179,183]

Alkoxyphenyl-, benzyloxyphenyl-, 3,4-di(hydroxymethyl)-phenyl-, and alkylthiophenyl-phosphonic acids have been synthesised from the corresponding diazonium salts and phosphorus trichloride in yields of 18–61%[173,174,184,185] and 2-phenoxyphenylphosphonic acid has been obtained in 63% yield.[186]

Arylphosphonic acids containing the carbonyl, sulphonamido-, and cyano-substituents, which are difficult to obtain by other methods, can be synthesised by the diazo-method in yields of 27–50%.[161,173,187]

Thus 2-carboxyphenylphosphonic acid has been obtained from the diazonium salt of anthranilic acid and phosphorus trichloride in one stage in a yield of 37%; previously its synthesis involved several stages.[173] The corresponding arylphosphonic acids have been synthesised in yields of 12–44% by this procedure from arenediazonium salts containing several different functional groups in the ring—one or two halogen (F, Cl, Br) atoms and the nitro-group,[163,173,184,188] a chlorine atom and the hydroxy-group[183] or the methoxy-group,[186] and the nitro and methoxy- or carboxy-groups.[173,177] For example, 2-methoxy-4-nitrophenylphosphonic acid has been obtained in 31% yield and used to synthesise 4-amino-2-hydroxyphenylphosphonic acid—the phosphorus analogue of 4-amino-salicyclic acid.[173]

It follows from the foregoing that the diazotisation method is simple to carry out and makes it possible to obtain arylphosphonic acids with a wide range of substituents in the aromatic ring, which are either difficult to obtain or cannot be obtained at all by other procedures. The disadvantages of the method include a comparatively low yield of the required substances, which rarely exceeds 50%, and its unsuitability for the synthesis of 2-nitro- and 2-hydroxy-phenylphosphonic acids as well as a number of other substituted arylphosphonic acids.

### 4. Arylation of Phosphorus Pentoxide and Pentasulphide

Aromatic compounds with hydroxy-, amino-, nitro-, and other groups which can undergo any kind of changes under the conditions of the synthesis are used as arylating agents in this procedure. The reaction is carried out in an autoclave at 150–225 °C using phosphorus pentasulphide and at 250–325 °C with phosphorus pentoxide, the reaction time being 5–25 h. The aromatic compound is taken in a large excess. The reaction products are hydrolysed with water to arylphosphonic acids. Thus, when anisole and phosphorus pentasulphide were used, 4-methoxyphenylphosphonic acid was obtained in 80% yield:[189–195]

$$RC_6H_5 + P_4X_{10} \xrightarrow{1)\,\Delta\ 2)\,H_2O,\,\Delta} RC_6H_4P(O)(OH)_2\ ;$$

R=H, $CH_3$, Cl, $OCH_3$, $OC_2H_5$; X=O, S .

The reaction proceeds with the preliminary dissociation of one bond in the hexagonal form of the phosphorus pentachalcogenide and the formation of a biradical or a dipolar ion, which then reacts with the aromatic compound to form the polymeric anhydrides of arylphosphonic or arylphosphonothioic acids.[189] Treatment of the anhydrides, thioanhydrides, and mixed thioanhydrides of the arylphosphonic acids with sulphuryl chloride, phosphorus pentachloride, or chlorine and then with sulphur dioxide leads to the dichlorides of arylphosphonic acids.[189,194,196–198] The latter can also be obtained by heating the aryl halides 4-$RC_6H_4Hal$ (R = H, $C_1$–$C_4$ alkyl or Cl and Hal = Cl, Br) directly with phosphorus pentoxide and phosphorus trihalide at 200–450 °C.[199]

When tetra-aryloxysilanes and triphenyl borate react with phosphorus pentasulphide, compounds (III) are formed and are then hydrolysed with water to hydroxyarylphosphonic acid in yields up to 40%:[200,201]

$$(RC_6H_4O)_nZ + P_4S_{10} \xrightarrow{170^\circ} \left\{\left[-S-\overset{\overset{S}{\|}}{\underset{|}{P}}(R)\,C_6H_3O\right]_nZ\right\}_2 \xrightarrow{H_2O,\,\Delta}$$

(III)

$$\rightarrow 4\text{-}HO(R)\,C_6H_3PO_3H_2\ ;$$

R=H, 3-$CH_3$; $n=3$, Z=B; $n=4$, Z=Si .

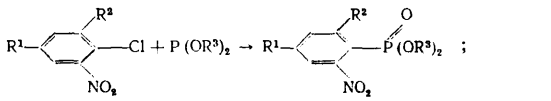
As a result of limitations in the choice of substituents in the benzene ring and preparative difficulties, the above procedure has not received extensive recognition.

### 5. Arylation of Phosphite Esters by Aryl Halides

This Section describes the methods of synthesis of neutral esters of arylphosphonic acids with different substituents in the ring by arylating the esters of phosphorous acids by aromatic halides or nitro-compounds.

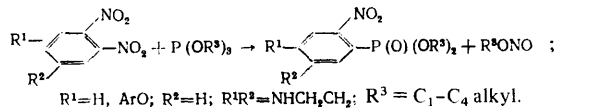
#### (a) Arylation without Initiators

4-Substituted tetrafluorophenylphosphonates have been obtained in 25–30% yields by the prolonged (16 h) heating (to 150 °C) in an autoclave of substituted pentafluorobenzenes ($RC_6F_5$, where R = H, $CF_3$, CN, $NO_2$, or $C_6F_5$) and triethyl phosphite.[202,203] When nitro-groups are present in the benzene ring in addition to the halogen atom, the reaction takes place at low temperatures (60–120 °C) with retention of the nitro-group and yields of the phosphonate up to 95%:[204–208]



$R^1$=H, $CF_3$, Cl, CN, $NO_2$, $C_2H_5SO_2$, $CH_3COO$; $R^2$=H, Cl, $NO_2$; $R^3 = C_1$–$C_4$ alkyl.

*o*-Dinitrobenzenes without a halogen arylate trialkyl phosphites in acetonitrile with formation of *o*-nitrophenylphosphonate in yields of 50–80%:[209–214]



$R^1$=H, ArO; $R^2$=H; $R^1R^2$=$NHCH_2CH_2$; $R^3 = C_1$–$C_4$ alkyl.

The nitro-group in 5(6)-nitrobenzimidazole is readily substituted by the phosphoryl group on heating with dialkyl phosphites.[215]

#### (b) Arylation in the Presence of Catalysts

Various arylphosphonates have been obtained in yields up to 90% by heating dialkyl phosphites[216–219] or trialkyl phosphites[220–234] with aryl halides in the presence of catalysts:

$$(R^1O)_2PONa + R^2Hal \xrightarrow{CuI} R^2P(O)(OR^1)_2 ;$$

$R^1$=$C_2H_5$, $C_6H_5$; $R^2$=$C_6H_5$, 4-$CH_3C_6H_4$, 4-$NH_2C_6H_4$, 2,4,6-$(CH_3)_3C_6H_2$, $(CH_3)_5C_6$; Hal=Br, I .

The best catalysts are nickel halides, used in an amount of 0.1–20 mole %,[220–225] and palladium chloride or acetate—0.01 0.01–0.05 mole %.[228,229] Copper bronze and copper(I) chloride give poorer results even when a threeefold excess of the phosphite is employed,[230,231] while alkylation in the presence of copper(I) iodide or copper acetate proceeds at comparatively low temperatures (0–115 °C) in a solvent, the yield of the phosphonates reaching 85%.[216,217,232–234] A complex of palladium halide with triphenylphosphine is also used as the catalyst.[218,219]

On heating to 250–340 °C in the presence of catalytic amounts of iodobenzene and nickel or copper halides, triphenyl phospite isomerises to diphenyl phenylphosphonate in yields up to 90%. In the presence of iron(III) chloride, less satisfactory results were obtained.[226]

The interaction of the sodium salts of dialkyl or diaryl phosphites with aryl halides takes place in the presence of copper(I) iodide or magnesium iodide. The yields of the arylphosphonates are 54–81%:[227,235]

$$R^1_nC_6H_{5-n}Hal + R^2OP(OR^3)_2 \rightarrow R^1_nC_6H_{5-n}P(O)(OR^3)_2 + R^2Hal ;$$

$n$=1, $R^1$=H, Cl, F, $CH_3$, $C_{12}H_{25}$, OH, $OCH_3$, $OC_6H_5$, $SCH_3$, $COCH_3$, $COOCH_3$, $COOC_2H_5$, $N(CH_3)_2$, $CH_2NH_2$, $NO_2$, CN; $n$ = 3, $R^1$=H, $CH_3$, $(CH_3)_3C$, OH, $NH_2$, $HNCOCH_3$, $N(C_2H_5)_2$, N=$NC_6H_3(R^1)N(C_2H_5)_2$; $R^2$=H, $R^3$; $R^3$=$CH_3$, $C_2H_5$, *изо*-$C_3H_7$; $R^1$=H, $CH_3$, $C_2H_5$, $NO_2$; Hal=Cl, Br, I.

#### (c) Arylation under Ultraviolet Irradiation

When a mixture of an aryl halide with a three-fivefold excess of trimethyl or triethyl phosphite is irradiated for a long time, dialkyl arylphosphonates are formed in a satisfactory yield. The optimum reaction temperature ranges from −5° to −25 °C. Aryl iodides or bromides are best as arylating agents. The dimethyl esters of phenyl-, tolyl-, and xylyl-phosphonic acids are obtained in yields of 50 to 100%. When triethyl phosphite is arylated, a more prolonged irradiation is required than in the arylation of trimethyl phosphite; with increase of the length of the group R in the phosphites $(RO_3)P$, the yield of aryl phosphonates is sharply reduced. Thus when tri-isopropyl phosphite and iodobenzene are used, the yield of di-isopropyl phenylphosphonate is only 26%.[236–242]

The reaction of dihalogenobenzenes and trimethyl phosphite affords dimethylhalogenophenyl phosphonates, the best yields (39–92%) having been achieved using 1,3- and 1,4-isomers and a combination of halogens: I and Cl or Br; Br and F. The side products of the reaction are phenylenediphosphonates, whose yield depends on the nature and positions of the halogen atoms in the dihalogenobenzene, reaching 87% when 1,2-bromoiodobenzene is employed and 10–39% in the case of the 1,3- and 1,4-isomers.[239,240] Pentafluoro- and pentachloro-pyridines interact with the lowest phosphites to form tetrahalogenopyridylphosphonates.[241]

Various isomers of methoxy- and dimethoxy-phenylphosphonic acids,[238,242,243] hydroxyphenylphosphonic acid,[238,242] aminophenylphosphonic acid,[244] formylphenylphosphonic acid,[243] and ethoxycarbonylphenylphosphonic acid[245] have been obtained by the reaction of substituted iodobenzenes with lower trialkyl phosphites in 34–92% yields. This method proved to be unsuitable for the synthesis of nitrophenylphosphonates because of the occurrence of oxidation-reduction processes in the interaction of nitrobenzene with phosphites.[238]

The sodium or potassium salts of dialkyl phosphites and *NNN'N'*-tetra-alkylphosphorodiamidous acids interact with aryl bromides or, better, iodides in liquid ammonia on irradiation with UV light with formation of phosphonates in 87–96% yield. Without illumination, the yield of the required compound is very low (0–7%):[246–252]

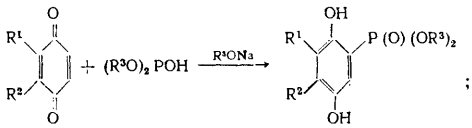
$$R^1_nC_6H_{5-n}Hal + MOPR^2_2 \rightarrow R^1_nC_6H_{5-n}P(O)R^2_2 ;$$

$n$=1, $R^1$=H, $CH_3$, $CF_3$, F, Cl, Br, I, OH, $NH_2$, $CONH_2$, $OCH_3$, $COOC_2H_5$; $n$=2, $R^1$=$CH_3$; $R^2$=$OCH_3$, $OC_2H_5$, $N(CH_3)_2$; Hal=Cl, Br; M=K, Na .

Under the same conditions, 1,3-dibromo- and 1,3-chloroiodobenzenes react with alkali metal salts of dialkyl phosphites, forming preferentially the tetra-alkyl esters of 1,3-phenylenebisphosphonic acids.[253,254] Instead of liquid ammonia, it is also possible to use other solvents (dimethyl sulphoxide, dimethyl formamide, t-butyl alcohol, and acetonitrile).[255]

### 6. Other Methods

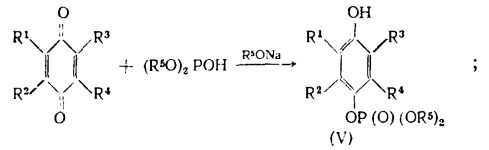
In the first communication[256] on the interaction of *p*-quinones with dialkyl phosphites in the presence of bases, it was suggested that the reaction product has the phosphonate structure (IV):



(IV)

$R^1=R^2=H$; $R^1R^2=(CH)_4$; $R^3 = C_1$-$C_{20}$ alkyl.

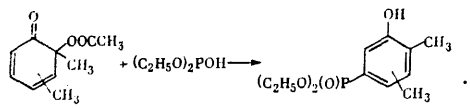
In subsequent studies[257–261] evidence was obtained showing that the product of this reaction is the phosphate (V):



(V)

$R^1=R^2=R^3=R^4=H$, Cl; $R^1=R^2=H$; $R^3R^4=(CH)_4$; $R^5=CH_3$, $C_2H_5$ .

The interaction of dimethyl phosphite with *p*-benzoquinone, which leads to the formation of a mixture of 55% of the phosphonate (IV, $R^1 = R^2 = H$, $R^3 = CH_3$), 10% of the phosphate (V, $R^1 = R^2 = R^3 = H$, $R^5 = CH_3$), and 8% of the bisphosphonate [IV, $R^1 = H$, $R^2 = P(O)(OCH_3)_2$] was later described.[262] The interaction of *p*-benzoquinone-bisbenzenesulphonyl imide with lower dialkyl phosphites also leads to a mixture of a phosphonate and a phosphoramidate whose ratio varies with the reaction conditions.[263] 3-Hydroxyarylphosphonates have been obtained in yields up to 40% by the reaction of substituted 2-acetoxy-2-methylcyclohexa-3,5-dienones with diethyl phosphite:[264]



In the study of the interaction of *p*-quinones with lower trialkyl phosphites, different workers also obtained contradictory data. Thus it has been claimed[265,266] that the products of this reaction are 2-alkoxy-5-hydroxyphenylphosphonates, in other investigations[267–269] the products were believed to be 4-alkoxyphenyl phosphates, while in yet another study[270] they were said to be 4-alkoxyphenyl phosphates with an admixture of 2,5-dihydroxyphenylphosphonate (up to 2%). The reaction of triethyl phosphite with benzoquinone and hydrogen chloride in ether at −70 °C leads to a 1:1 mixture of the phosphate and phosphonate.[271]

When aryl 4-bromophenyl sulphides or aryl 4-bromophenyl ethers are heated with equimolar amounts of phosphorus trichloride and aluminium chloride with subsequent alkaline hydrolysis, the phosphonic acids $ArXC_6H_4PO_3H_2$-4 are formed in 75–90% yields for X = O and 12.5–67% yields for X = S and Ar = $C_6H_4R^2$-4; $R^2 = CH_3$, F, Cl, or Br.[148,149]

The electrochemical oxidation of a mixture of trialkyl phosphite and an 18–25-fold excess of an aromatic hydrocarbon in acetonitrile at room temperature results in the formation of dialkyl arylphosphonates in 14–66% yields:[272–276]

$$(R^1O)_3P + R^2_nC_6H_{6-n} \rightarrow (R^1O)_2P(O)C_6H_{5-n}R^2_n ;$$

$R^1 = C_1$-$C_3$ alkyl; $R^2 = H$ or $C_1$-$C_4$ alkyl; $n = 1, 2$.

When benzene or chlorobenzene was heated with phosphorus trichloride and benzoyl peroxide, the dichlorides of phenyl- and chlorophenylphosphonic acids were obtained respectively.[277] The interaction of dialkyl phosphites with benzoyl peroxide leads to the formation of 4-carboxyphenyl phosphonates in 55% yield.[278,279] In the presence of t-butyl peroxide, dialkyl phosphites react with aromatic hydrocarbons. After the acid hydrolysis of the reaction products, aryl phosphoric acids are obtained in yields up to 65%:[280,281]

$$R^1C_6H_4R^2 + (R^3O)_2POH \xrightarrow[1,\ \Delta\ 2)\ HCl]{[(CH_3)_3CO]_2} R^1(R^2)C_6H_3P(O)(OH)_2 ;$$

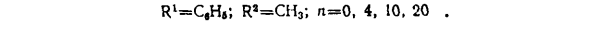
$R^1$=H, $CH_3$, $CH_3O$, Br, $CH_3OOC$; $R^2$=H, $CH_3$; $R^1R^2=(CH)_4$; $R^3=CH_3$, $C_2H_5$.

In the presence of strong bases, for example, lithium di-isopropylamide, dialkyl phenyl phosphate rearranges to 2-hydroxyphenylphosphonate in yields up to 98%.[282] The diethyl esters, ester-amides, and diamides of arylphosphonic acids, containing various substituents have been synthesised by the reaction of aryl-lithium or arylmagnesium halides with dialkyl phosphorochloridates in yields of 5.7–65.4%[225,243,289–293] and with phosphorodiamidic chlorides in yields of 18–75.2%.[290,291] 2,5-Dichlorophenyl (*N*-isopropyl)phenylphosphonamidate has been obtained in 26.6% yield.[292] The reaction is carried out in absolute ether or tetrahydrofuran:

$$R^1_2P(O)Cl + R^2_nC_6H_{5-n}M \rightarrow R^1_2P(O)C_6H_{5-n}R^2_n ;$$

$R^1$=$CH_3O$, $C_2H_5O$, $NHC_6H_5$, $NC_5H_{10}$; $R^2$=H, $CH_3$, $CH_3O$, Cl, Br, $C_6H_5$, $(CH_3)_3SiCH_2$, $(CH_3)_3Si$, $C_4H_9SCH_2$; $n = 1, 2$:
M=Li, MgCl, MgBr .

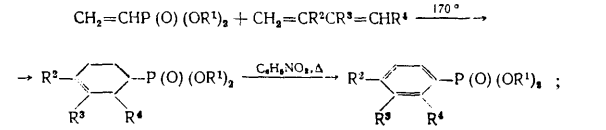
Bisphosphorylated siloxanes have been obtained in this way from diphenyl phosphorochloridate in siloxanes containing two phenylmagnesium bromide groups at different silicon atoms:[293,294]



$R^1=C_6H_5$; $R^2=CH_3$; $n$=0, 4, 10, 20 .

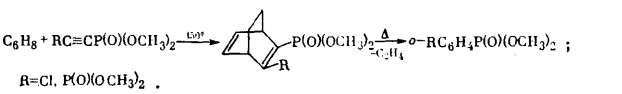
Tetraphenyl-lead or tetraphenyl–tin arylate phosphoryl chloride on prolonged (130–180 h) heating (to 180 °C) with formation of phenylphosphonic dichloride in yields up to 58%.[121,122]

The diene synthesis reaction is sometimes used to obtain the esters of arylphosphonic acids. Thus arylphosphonates have been obtained in yields up to 68% from diethyl vinylphosphonate and substituted butadienes with subsequent dehydrogenation of the reaction products.[295]



$R^1=C_2H_5$; $R^2$, $R^3$=H, $CH_3$; $R^4=R^2$, $CH_3O$ .

2-Substituted dimethyl arylphosphonates are obtained from cyclohexadiene and dimethyl chloroethynylphosphonate or tetramethyl ethynylenediphosphonate. The reaction involves the formation of a bicyclic phosphonate which splits off ethylene at a high temperature and affords the aryl phosphonate:[296]



R=Cl, $P(O)(OCH_3)_2$ .

2,5-Diphenylphenylphosphonic acid is obtained from maleic anhydride and 3-(2,5-diphenylfuryl)phenylphosphonic acid in 10–15% yield.[170] Dialkyl 5-acyl-2-isopropyl-4-methylphenylphosphonate has been obtained by heating dialkyl 3,3-dimethyl-1-vinylallenylphosphonate and acetylacetone in the presence of sodium ethoxide.[297]

## III. METHODS OF SYNTHESIS OF ARYLPHOSPHONOTHIOIC ACIDS AND THEIR DERIVATIVES

Few methods are available for the synthesis of arylphosphonothioic acids and their derivatives and the choice of substituents in the aromatic ring (namely alkyl, alkoxy-, or halogeno-groups) is limited.

The dichlorides of arylphosphonothioic acids $R_nC_6H_{5-n}\cdot P(S)Cl_2$ ($R = C_1-C_{30}$ alkyl, F, Cl, Br, or $CF_3$ and $n = 1$ or 2) are obtained by adding sulphur to the aluminium chloride complex of an aryldichlorophosphine[95,298-300] or to free aryldihalogenophosphines in the presence of catalytic amounts of aluminium chloride[25,301] and ammonium or phosphonium salts.[302]

Successive treatment of dichlorophenyl- or chlorophenyldichlorophosphines with sulphur monochloride and sulphur dioxide or phosphorus pentoxide yields a mixture of the dichlorides of the corresponding arylphosphonic and arylphosphonothioic acids with the latter predominating.[303] On heating with thiophosphoryl chloride, 4-chlorophenyldichlorophosphine is converted into the dichloride of 4-chlorophenylphosphonothioic acid in 93.1% yield.[304] The esters, amides, and anhydrides of arylphosphonothioic acids are obtained by adding sulphur to the corresponding derivatives of arylphosphonous acids in yields up to 90%[5,34,43,104,304-306] or by oxidising the esters of arylphosphonothious acids with hydrogen peroxide.[305] The dihalides of arylphosphonothioic acids are obtained in yields of 10–79% on heating thiophosphoryl halide and an aromatic hydrocarbon with aluminium and aluminium chloride[307-311] or by heating an aromatic hydrocarbon with aluminium chloride, phosphorus trihalide, and phosphorus pentasulphide:[309,310,312-316]

$$RC_6H_5 + PSHal_3 \xrightarrow{AlCl_3,\ \Delta} RC_6H_4P(S)Hal_2 ;$$
$$R=H,\ CH_3,\ F,\ Cl;\ Hal=Cl,\ Br .$$

When aluminium chloride is used, the $PSHal_3 : AlCl_3 : ArH$ reactant molar ratios are 1:2–2.5:1–1.1. The side products are the halides of diarylphosphinothioic acids and triarylphosphine sulphides, whose amount increases with increase of the reaction time as the reactant ratio is altered. Thus, after the reactant mixture had been refluxed for 4 h, the above two impurities were isolated in yields of 30 and 70% ($Ar = C_6H_{13}C_6H_4$).[315,316]

The phosphorylation of aromatic hydrocarbons by thiophosphoryl halides[317-320] or by a mixture of phosphorus trihalide and sulphur[321] as well as the phosphorylation of aryl halides by phosphorus sulphide ($P_4S_3$) [322] or mixtures of phosphorus sulphide ($P_4S_{10}$) with phosphorus trihalides[199,323] containing red phosphorus,[324] thiophosphoryl halides,[325] or thiophosphoryl halides and red phosphorus[326] as additives leads to the formation of the dihalides of arylphosphonothioic acids $RnC_6H_{5-n}P(S)Hal_2$ ($R = H$, $C_1-C_4$ alkyl, F, or Cl; $n = 1$ or 2; Hal = Cl or Br). The same products have been obtained by phosphorylating aryl halides with a mixture of thiophosphoryl halide with white or red phosphorus[327,328] or a mixture of phosphorus trihalide with phosphorus and sulphur.[329] The yield of the products is 35–87%. All these reactions take place at 200–450 °C. The reaction temperature falls following the addition of iodine, metal iodides, and alkyl iodides in an amount equivalent to 0.01–0.1% of the weights of the reaction mass.[323,327] The phosphorylation of toluene affords a mixture containing equal amounts of the dihalides of 4-tolylphosphonothioic and benzylphosphonothioic acids.[317-319]

The tetrachlorides of 1,4-arylenebis(phosphonothioic) acids are formed in 60–66% yield when 1,4-dichlorobenzene is heated with phosphorus trichloride and pentasulphide or with thiophosphoryl chloride and white phosphorus.[323,324,327,329]

The dihalides of arylphosphonothioic acids are obtained in 30–91.2% yields when an excess of phosphorus trihalide is heated with di- and tri-aryl phosphorothioites,[330-332] triaryl phosphorotetrathioates,[333] and diaryl sulphides[334,335] and disulphides[336] at 250–600 °C in the presence of catalytic amounts of halogens, halogeno-containing heterocarbons, metal halides, or without a catalyst. The halides of diarylphosphinothioic acids are formed as side products. For example:

$$(R_nC_6H_{5-n}S)_3P + PHal_3 \xrightarrow{\Delta} R_nC_6H_{5-n}P(S)Hal_2 + (R_nC_6H_{5-n})_2P(S)Hal ;$$
$$n=1,\ R=CH_3,\ (CH_3)_3C,\ C_9H_{19};\ n=2,\ R=Hal;\ Hal=Cl,\ Br ;$$

$$(R_nC_6H_{5-n})_2S + PHal_3 \xrightarrow{\Delta} R_nC_6H_{5-n}P(S)Hal_2 + (R_nC_6H^{5-n}_2)P(S)Hal ;$$
$$R=CH_3,\ C_2H_5;\ n=1-3;\ Hal=F,\ Cl,\ Br .$$

A mixture of phosphorus trihalide with white phosphorus[337,338] or with thiophosphoryl halide and phosphorus sulphides (of the type $P_4S_n$, where $n = 3$, 5, 7, or 10) has been introduced into the reaction with diaryl sulphides and disulphides.[339] The dichlorides of arylphosphonothioic acids are also formed in 65–90% yield when phosphorus trichloride is heated with arenethiols at 250–320 °C, but this requires the preliminary refluxing of the mixture of the initial reactants at atmospheric pressure:[340]

$$R_nC_6H_{5-n}SH + PCl_3 \rightarrow R_nC_6H_{5-n}P(S)Cl_2 ;$$
$$R=H,\ Cl,\ (CH_3)_3C;\ n=1-5 .$$

The thioanhydrides of arylphosphonothioic acids are obtained in 53.2–99% yield when a tenfold excess of *o*-xylene, anisole, and phenetole is heated with phosphorus pentasulphide[191,194,201,341,342] or with a mixture of phosphorus (white or red) and sulphur:[343-345]

$$R_nC_6H_{6-n} + P_4S_{10} \xrightarrow{150-170^\circ C} (R_nC_6H_{5-n}PS_2)_2 ;$$
$$n=1,\ R=CH_3O,\ C_2H_5O;\ n=2,\ R=CH_3 .$$

The dihalides of arylphosphonothioic acids are formed in 73–90% yield when the thioanhydrides of arylphosphonothioic and arylphosphonothious acids are treated with halogens and phosphorus pentachloride.[43,194,198]

On heating with thiophosphoryl halide, phosphorus pentasulphide,[346,347] white phosphorus, and sulphur,[348] the dihalides of arylphosphonic acids are converted into the dihalides of arylphosphonothioic acids.

The ester-halides of arylphosphonodithioic acids are formed when aryldihalogenophosphines react with sulphenyl chloride and hydrogen sulphide:[349,350]

$$ArPHal_2 \xrightarrow[2)\ H_2S]{1)\ ClSCH_2CH_2OR} ArP(S)(SCH_2CH_2OR)Hal .$$

They are also formed when the above compounds are heated with sulphenyl chloride in liquid sulphur dioxide or glacial acetic acid in the absence or presence of an inert solvent (methylene chloride or chloroform) at temperatures between −40° and 35 °C:[351-354]

$$R^1C_6H_4PCl_2 + R^2SCl \xrightarrow{CH_3COOH} R^1C_6H_4P(O)(SR^2)Cl ;$$
$$R^1=F,\ Cl;\ R^2 = \text{alkyl},\ CH_2CH=CH_2,\ CH_2C_6H_5,$$
$$CH_2CH_2OCH_3,\ CH_2CH_2OAr .$$

The ester-chlorides are usually not isolated but are converted into esters and ester-amides of arylphosphonothiolic and arylphosphonodithioic acids in 70–90% yield by reactions with alcohols, mercaptans, and amines. The simultaneous addition of dichlorophosphine and sulphenyl chloride to an excess of the alcohol in the solvent leads to *OS*-dialkyl (or alkyl aryl) arylphosphonothiolates in 66–99% yield:[144]

$$R^1C_6H_4PCl_2 + R^2SCl + R^3OH \xrightarrow{-40^\circ C} R^1C_6H_4P(O)(SR^2)(OR^3) ;$$
$$R^1=F,\ Cl;\ R^2 = C_1-C_5\ \text{alkyl},\ C_6H_5;\ R^3=CH_3,\ (CH_3)_2CH .$$

The diethyl esters of 2,3,5,6-tetrafluoroarylphosphonothioic acids are formed in 37–41% yield when pentafluorobenzene derivatives are heated with sodium diethyl phosphorothioite in tetrahydrofuran.[335]

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# The Reactivity of Organozinc and Organocadmium Compounds in Decomposition Reactions

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The literature data on the thermal decomposition and photodecomposition of organozinc and organocadmium compounds, on the dependence of the thermal decomposition mechanism and the kinetic stability of metal alkyls in this reaction on the decomposition conditions, and also on the relation between the reactivity of the organometallic compounds and their structure are treated systematically and discussed.
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## I. INTRODUCTION

The thermal decomposition reactions of organozinc and organocadmium compounds are of interest in connection with problems of the formation of zinc and cadmium coatings by chemical deposition from the gas phase.[1] Nevertheless the relevant literature data have not been subjected to systematic analysis.[1,2]

The lower alkyl derivatives of Group IIB metals are extremely unstable[3] and their use has until recently been limited.[4] However, during the last decade the dialkyl compounds of zinc and cadmium have found applications in the preparation of metallic and semiconductor coatings.[5-14] The use of metal alkyls in semiconductor technology has stimulated further research into the kinetic and thermodynamic stabilities of these organometallic compounds (OMC) and into the improvement of the methods of their synthesis[15,16] and analysis[17,18] in order to obtain specially pure compounds and also to develop conditions for the deposition and segregation of the condensed phase of the metal on thermal decomposition of the OMC.[19]

The existing reviews on the reactions involving the homolytic cleavage of organometallic compounds[20-24] are mainly concerned with OMC about the decomposition of which more reliable data are available (mercury, lead, tin, bismuth, antimony, gallium, arsenic, and titanium). It appears useful to discuss separately the results of experimental studies on the homolytic decomposition of organozinc and organocadmium compounds. This review presents a systematic account and a survey of data on the kinetic stability of the zinc and cadmium OMC in photodecomposition and thermal decomposition reactions.

## II. KINETICS AND MECHANISMS OF THE DECOMPOSITION OF ORGANOZINC AND ORGANOCADMIUM COMPOUNDS

### 1. Decomposition of Organozinc Compounds

Although the pyrolysis of metal alkyls with formation of the corresponding metals and radicals has been known since Paneth's classical studies, the kinetic investigations of these processes began only two decades ago and have not been systematic.[1] The kinetics of the gas-phase pyrolysis of dimethylzinc in a static system have been studied over a wide range of initial reactant pressures from 15 to 580 mmHg at temperatures in the range 280–340 °C.[25,26] It has been observed[25] that the rate of decomposition diminishes with increase of the initial pressure of dimethylzinc and that there is a simultaneous increase of the yield of the main gaseous product—methane. At a single fixed initial pressure the rate of decomposition and the yield obtained increase with increasing ratio of the reactor surface area S to the reactor volume V (the so-called heterogeneous factor $S/V$). In the high-temperature region a narrow pressure range has been found (27–55 mmHg) in which the decomposition rate constant is invariant and corresponds to a first-order kinetic law. It has been suggested that part of the methane is produced heterogeneously, although the contribution of the heterogeneous component of the reaction has not been established and the kinetic parameters of the overall reaction have not been calculated. It has been suggested that methane and ethane are formed in the stages involving the methyl radical-induced decomposition of dimethylzinc and the dimerisation of the methyl radicals respectively. Metallic zinc and polymethylene have been detected in addition to the gaseous products.

Self-inhibition of the reaction was observed in a later study.[26] The nature of the self-inhibition was not elucidated, but, by analogy with the cracking of hydrocarbons, it was postulated that it is caused by the addition of the methyl radical to the double bond in the ethylene formed with formation of a less reactive radical. The self-inhibition coefficient is independent of pressure and temperature.

The effective decomposition rate constant depends on the initial OMC concentration but a definite relation has not been observed. The effective activation energy diminishes with increase of the dimethylzinc concentration. A radical-chain mechanism of the thermal decomposition of dimethylzinc *in vacuo* under static conditions has been proposed:

$$Me_2Zn \rightarrow Me + {}^{\cdot}ZnMe, \qquad (1)$$

$$\begin{gathered}
{}^{\cdot}ZnMe \rightarrow Zn + Me, \\
Me + Me_2Zn \rightarrow CH_4 + {}^{\cdot}CH_2ZnMe, \\
{}^{\cdot}CH_2ZnMe \rightarrow :CH_2 + Zn + Me, \\
:CH_2 + Me_2Zn \rightarrow EtZnMe \rightarrow Et + {}^{\cdot}ZnMe, \\
2Me \rightarrow C_2H_6, \\
Me + {}^{\cdot}CH_2ZnMe \rightarrow CH_4 + C_2H_4 + Zn, \\
Me + Et \begin{cases} \rightarrow C_3H_8, \\ \rightarrow CH_4 + C_2H_4. \end{cases}
\end{gathered} \qquad (2)$$

The following compounds were found among the gaseous pyrolysis products (mole %): methane 88.0, ethane 4.2 to 5.5, propane 4.0–5.9, butane 1.2–1.4, ethylene 0.2–0.6, and propene 0.5–1.5.[26]

Methane is the only gaseous product of the decomposition of dimethylzinc in a sealed tube in the presence of cyclohexane (250–400 °C, pressure close to atmospheric).[27] With decrease of the fraction of cyclohexene, ethane and propane appear in the mixture of decomposition products. The following process mechanism in the presence of excess cyclohexane has been proposed:

$$Me_2Zn \rightarrow Me + ZnMe ,$$
$$Me + C_6H_{12} \rightarrow CH_4 + {}^{\cdot}C_6H_{11} ,$$
$$2{}^{\cdot}ZnMe \rightarrow ({}^{\cdot}ZnMe)_2 .$$

The activation energy for the first of these reactions has been determined as 45.5 ± 3.3 kcal mol$^{-1}$.

The use of cyclohexane in a fully deuteriated form permitted the conclusion that, under the given experimental conditions, the role of the induced decomposition reaction $Me + Me_2Zn \rightarrow CH_4 + {}^{\cdot}CH_2ZnMe$ is small even in the total absence of cyclohexane. The estimated activation energy for this reaction is ≥15 kcal mol$^{-1}$.[27]

The induced decomposition of dimethylzinc was fully eliminated when the reaction was carried out under flow conditions in the presence of an excess of toluene.[28] The following mechanism, analogous to the mechanisms of the decomposition of dimethylcadmium and dimethylmercury,[29] has been proposed for the decomposition of dimethylzinc under these conditions:

$$Me_2Zn \rightarrow Me + {}^{\cdot}ZnMe , \quad (1)$$

$${}^{\cdot}ZnMe \rightarrow Me + Zn , \quad (2)$$

$$Me + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2^{\cdot} , \quad (3)$$

$$2Me \rightarrow C_2H_6 ,$$
$$2C_6H_5CH_2^{\cdot} \rightarrow (C_6H_5CH_2)_2 . \quad (4)$$

Reaction (2) does not occur at temperatures below 670 °C. It begins to play an appreciable role only above 730 °C but is complicated by the decomposition of toluene. For this reason, in the temperature range 573–700 °C it was possible to investigate the kinetics of the radical initiation reaction (1). The kinetic parameters of reaction (2) were obtained after applying a correction taking into account the yield of methane resulting from the decomposition of toluene. Both rate constants, $k_1$ and $k_2$, depend appreciably on the pressure in the system. At a fixed pressure of 16 mmHg, the following expressions were obtained for the rate constants for the elementary reactions (1)–(4):[28]

$$\lg k_1, (s^{-1}) = 11.25 - (47\,200 \pm 1000)/4.58T ;$$
$$\lg k_2, (s^{-1}) = 6.8 - 35\,000/4.58T ;$$
$$\lg (k_3/k_4^{1/2}), (mol^{-1/2})\ cm^{3/2}\ s^{-1/2} = 6.3 - 13\,000/4.58T .$$

At an overall pressure of 5 mmHg, the expression for the $k_1$ becomes[28]

$$\lg k_1, (s^{-1}) = 11.03 - 47\,300/4.58T .$$

If the reverse radical recombination reactions do not require an activation energy, the activation energies obtained for the forward reactions (1) and (2) can be regarded as equal to the dissociation energies $D_1$ and $D_2$ of the MeZn–Me and Zn–Me bonds respectively. It has been shown[28] that the thermochemical estimate $D_1 + D_2 = 82.9$ kcal mol$^{-1}$ agrees with kinetic data.

The gas-phase decomposition of diethylzinc does not have the distinctive features which characterise the pyrolysis of the methyl derivative (the dependence of the rate constant and the activation parameters on the initial reactant concentration and the self-inhibition of the reaction).

In an early study of the photolysis of diethylzinc,[30] the reactivity of the ethyl radicals formed in the primary decomposition step was investigated. At a pressure of 25 mmHg and in the temperature range 45–250 °C, ethane, ethylene, butane, and traces of hydrogen, butene and higher hydrocarbons were detected in the reaction products. The study of the influence of changes in the concentration of diethylzinc, the radiation intensity, the packing of the reaction vessel comprising an inert phase, and the pressure of an inert gas on the composition of the product led to the conclusion that butane is the product of the recombination of two ethyl radicals, while ethane and ethylene are formed as a result of the interaction of ethyl radicals with a molecule of the metal alkyl. The rate of the reaction of ethyl radicals with hydrogen becomes significant above 160 °C and its activation energy has been estimated as 9 ± 2 kcal mol$^{-1}$. The composition of the photolysis products at high temperatures is analogous to the composition of the thermal decomposition products.

Kinetic studies of the pyrolysis of diethylzinc have been carried out in a stream of toluene[31] and an inert gas,[32] in a static system,[32,33] and in a molecular beam.[33,34]

A free-radical mechanism has been proposed for the decomposition of diethylzinc in a stream of toluene, analogous to that described above for dimethylzinc, but it is more detailed as regards the reaction of all the radicals formed in the system.[31] In the mechanism of the multistage generation of radicals of diethylzinc, the second stage ${}^{\cdot}ZnEt \rightarrow Zn + Et$ is very rapid, in contrast to the reaction ${}^{\cdot}ZnMe \rightarrow Zn + Me$. The absence of induced decomposition in a stream of toluene made it possible to determine the kinetic and activation parameters for the first stage of the homogeneous initiation of radicals via the reaction $Et_2Zn \rightarrow Et + {}^{\cdot}ZnEt$ (Table 1). The presence of zinc oxide on the reactor surface greatly accelerated this reaction, which indicates a sensitivity to the nature of the surface.

The decomposition of diethylzinc under dynamic conditions in a stream of helium in tubular reactors with the surface coated by the solid products of its pyrolysis[32] obeys the first-order kinetics. For short contact times in an open system, there is insufficient time for the development of the chain process. The experimental activation energy for the decomposition of diethylzinc in a stream of helium (47.6 kcal mol$^{-1}$) is close to the dissociation energy of the EtZn–Et bond which has been estimated[31] as 47.5 kcal mol$^{-1}$. Only the unduly large pre-exponential factor ($\lg A = 16.13$) in the expression for the rate constant for the pyrolysis of diethylzinc in a stream of helium precludes a reliable assignment of the activation parameters obtained to a specific stage of the decomposition process.

In a closed system, diethylzinc also decomposes in accordance with first-order kinetics.[32] In contrast to the methyl derivative, a wide range of pressures (50–175 mmHg) has been found for this compound in which the rate constant is invariant. On passing to atmospheric pressure, the reaction continues to be first order. An inhibiting effect by the decomposition products has not been observed. The reaction involving the formation of metallic zinc from diethylzinc in the presence of added hydrogen has been noted.

A satisfactory interpretation of the results has been achieved on the assumption of a radical-chain mechanism of the decomposition:[32]

$$Et_2Zn \rightarrow Et + {}^{\cdot}ZnEt , \quad (5)$$

$${}^{\cdot}ZnEt \rightarrow Et + Zn , \quad (6)$$

$$Et + Et_2Zn \rightarrow C_2H_6 + C_2H_4 + {}^{\cdot}ZnEt . \quad (7)$$

$$Et \rightarrow C_2H_4 + H^{\cdot}, \quad (8)$$

$$H^{\cdot} + Et_2Zn \rightarrow C_2H_6 + {}^{\cdot}ZnEt, \quad (9)$$

$$2Et \rightarrow C_4H_{10} \text{ (or } C_2H_6 + C_2H_4). \quad (10)$$

The experimental effective rate constant is $k_{eff} = k_8 \cdot (k_5/k_{10})^{1/2}\ s^{-1}$. The initiation stage (5) can occur on the surface, since zinc oxide has been found to have an accelerating effect, but the process is propagated in the bulk phase (because the ratio $S/V$ has not effect and acceleration of the reaction by added hydrogen is not observed).

In order to account for the overall first order of the reaction, it is necessary to assume that the initiation reaction (5) in the gas phase is of second order, although it is known that zinc alkyls are not associated in the gas phase.[35] However, it has been observed in the liquid-phase autoxidation of dimethylzinc[36] that the initiation of the radicals does indeed take place as a result of the interaction of two dimethylzinc molecules.

In contrast to the liquid-phase pyrolysis,[32,37] in the gas-phase pyrolysis the contribution of the disproportionation reactions to the formation of ethane and ethylene is small[38] and their rate is 0.11–0.14 of the rate of recombination of ethyl radicals.

It has been observed[32] that the ethylene formed can be consumed in secondary reactions involving insertion in the C–Zn bond in diethylzinc. Thus the hydrolysis in heavy water of the condensed residue after the interaction of diethylzinc with ethylene yielded, together with monodeuteriomethane, also monodeuteriobutane. At the same time, the absence of dideuterioethane in the same experiment shows that the intramolecular and intermolecular decomposition of diethylzinc via the α-disproportionation of the ethyl groups does not occur under the given experimental conditions. It was postulated[32] that in a closed system the main gaseous product, namely ethane, is formed preferentially in the induced diethylzinc decomposition reaction (7).

The following compounds were detected in the gaseous products of the total decomposition of diethylzinc under static conditions at 270 °C [32] (in moles per mole of the substance decomposed): octane 0.0010, octene 0.0023, hexane 0.0085, hexene 0.0142, butane 0.2219, butene 0.0619, ethane 1.0443, ethylene 0.2709, and hydrogen 0.1072. Metallic zinc was found in the solid phase.

High pressures (from tens mmHg to atmospheric pressure) and low degrees of decomposition favour the abstraction of hydrogen from the diethylzinc molecule by the ethyl radical formed in the primary decomposition step.[33] Decrease of the pressure to $10^{-4}$ mmHg tends to decrease the kinetic stability of zinc dialkyls.[34] Under dynamic conditions, on passing from atmospheric pressure in a stream of helium to a high vacuum, the temperature of the total decomposition of diethylzinc decreases on the zinc coating from 310° to 130 °C and on zinc oxide from 310° to room temperature. The lines due to the molecular ions in the mass spectrum of dimethylzinc decomposing under high vacuum conditions on the solid products of its pyrolysis disappear already at 230 °C. The apparent activation energies in the temperature range 100 to 300 °C are 7.7 ± 1.5 and 6 ± 1.0 kcal $mol^{-1}$ for dimethylzinc and diethylzinc respectively. The composition of the products changes significantly in the pyrolysis of diethylzinc *in vacuo*[34] and the gas phase becomes enriched to the extent of approximately 70% in ethylene as a consequence of the vigorous dehydrogenation of ethane on pyrolytic zinc at the instant of formation.

In a high vacuum, where contact of OMC molecules with one another and also with the thermal decomposition products and the carrier gas is ruled out, the reactant decomposes heterogeneously in the adsorbed state on the catalytic centres of the reactor surface.[34] It has been suggested that, under dynamic conditions in a high vacuum, zinc alkyls decompose intramolecularly in accordance with the following mechanism:

$$Me_2Zn \xrightarrow{\text{recombination}} C_2H_6;$$
$$Me_2Zn \xrightarrow{\alpha\text{-disproportionation}} CH_4 + CH_2{:}Zn;$$
$$Et_2Zn \xrightarrow{\beta\text{-disproportionation}} C_2H_4 + C_2H_6 + Zn_{abs}.$$

**Table 1.** Activation parameters of the stages in the gas-phase pyrolysis of zinc dialkyls.

| Condition | Stage | $E$, kcal $mol^{-1}$ | lg$A$ | Refs. |
|---|---|---|---|---|
| | Dimethylzinc | | | |
| 16 mmHg, 573–700°, toluene stream | $Me_2Zn \rightarrow Me + ZnMe$ | 47.2±1.0 | 11.25 | [28] |
| 5 mmHg, 573–700°, toluene stream | $Me_2Zn \rightarrow Me + ZnMe$ | 47.3 | 11.03 | [28] |
| 16 mmHg, 730–825°, toluene stream | $Me \rightarrow Me + Zn$ | 35.0 | 6.8 | [28] |
| 1 atm, 250–400°, in the presence of cyclohexane, static system | $Me_2Zn \rightarrow Me + ZnMe$ | 45.5±3.3 | — | [27] |
| 580 mmHg, 280–338°, static system | overall process | 35.0±1.5 | 9.63±0.02 | [26] |
| $10^{-4}$ mmHg, 170–230°, molecular beam | overall process | 7.7±1.5 | — | [34] |
| | Diethylzinc | | | |
| 15 mmHg, 440–473°, toluene stream | $Et_2Zn \rightarrow Et + ZnEt$ | 49.0±2.0 | 14.3±0.6 | [31] |
| Ditto | $Et_2Zn \rightarrow Et + ZnEt$ * | 24.0±5.0 | 7.6±1.6 | [31] |
| 150–175 mmHg, 270–310°, static system | overall process | 28.3±0.3 | 8.44±0.13 | [32] |
| 1 atm, 310–340°, helium stream | overall process | 47.6±2.5 | 16.13±0.93 | [32] |
| $10^{-4}$ mmHg, 80–130°, molecular beam | overall process | 6.0±1.0 | — | [34] |

*In the presence of zinc oxide.

**Table 2.** The influence of the reaction conditions on the mechanism of the gas-phase decomposition of zinc dialkyls.

| System | Reaction conditions | Decomposition mechanism | Refs. |
|---|---|---|---|
| | | Dimethylzinc | |
| Static* | 305–340°, 13–270 mmHg | radical, with selfinhibition | [25] |
| | 280–338°, 580 mmHg | radical, with selfinhibition | [26] |
| | 250–400°, atmospheric pressure, in the presence of cyclohexane | radical | [27] |
| Toluene stream** | 573–700°, 16 mmHg | radical, $k_{exp} = k_1$ ($s^{-1}$) ($e^{-1}$) | [28] |
| | 730–825°, 16 mmHg | radical, $k_{exp} = k_2$ ($s^{-1}$) ($e^{-1}$) | [28] |
| Molecular beam | 170–230°, $10^{-4}$ mmHg | intramolecular heterogeneous (recombination and α-disproportionation); $E_{app} \ll E_{hom}$ | [24] |
| | | Diethylzinc | |
| Static* | 270–310°, 50–170 mmHg | radical-chain: $k_{exp}$ ($s^{-1}$) $= k_8(k_5/k_{10})^{1/2}$; $k_5$ – second order reaction | [32] |
| Toluene stream** | 440–483°, 15 mmHg | radical non-chain: homogeneous $k_{exp} = k_5$ ($s^{-1}$); heterogeneous (on ZnO) $k_{exp} = k_5$ ($s^{-1}$); $k_5$ – first order reaction | [31] |
| Helium stream** | 310–340°, atmospheric pressure | radical non-chain: $k_{exp}$ – first order reaction | [32] |
| Molecular beam | 90–150°, $10^{-4}$ mmHg | intramolecular heterogeneous (β-disproportionation); $E_{app} \ll E_{hom}$ | [33,34] |

*In a glass reactor.
**The reactor walls were coated by the solid pyrolysis products.

The kinetic stability and mechanism of the pyrolysis of zinc alkyls depend on the decomposition conditions. The free-radical mechanism operates at reduced and atmospheric pressures, while the molecular mechanism, characteristic of the adsorbed state, operates in a high vacuum (Table 2).

The homolytic reactions of organozinc compounds (the methyl, ethyl and phenyl derivatives) in the liquid phase and in solution in benzene in the course of their thermal decomposition and photodecomposition have been described.[39–44] The decomposition proceeds via a free-radical mechanism and is accompanied by the formation of a metallic mirror and the segregation of radical reaction products. The radical disproportionation and dimerisation reactions are characteristic of the photolysis (20–30 °C). The thermal decomposition of the OMC in the absence of a solvent entails, apart from the above reactions, the interactions of the alkyl radicals with the hydrocarbons and the initial OMC. In the solvent, the reaction takes place mainly via the mechanism involving the homolytic substitution of hydrogen in the solvent molecules by the alkyl or phenyl radicals formed.

The disproportionation and recombination reactions of the alkyl radicals are the most characteristic of the liquid-phase decomposition of the OMC, in contrast to the gas-phase decomposition, the contribution of the disproportionation to the thermal decomposition increasing with increase in the complexity of the radical on going from ethyl[45] to pentyl[46] radicals.

A method has been proposed for the preparation of zinc and cadmium coatings with a thickness up to tens of microns by the decomposition of zinc dialkyls (at 310–330 °C) and cadmium dialkyls (at 230–290 °C) by a gas-thermal method.[47] The coatings constitute a dense polycrystalline film with a grain size of approximately 1–5 μm.

## 2. Decomposition of Organocadmium Compounds

The gas-phase pyrolysis of dimethyl cadmium has been investigated under static conditions[48,49] in a stream of toluene[29] and benzene.[50] In an early study[48] measurements were made of the initial rates of formation of the principal gaseous pyrolysis products—methane and ethane. A poor reproducibility of the results was noted and considerable surface effects were observed, although the cadmium and polymethylene formed did not alter the rate of reaction. The increase of the heterogeneous factor (i.e. the increase of $S/V$) diminishes the rate of formation of ethane and methane, while the addition of hydrogen, nitrogen, helium, and nitric oxide increases them. As an alternative to the generally accepted free-radical mechanism, observed in the photolysis and thermolysis of metal alkyls, a mechanism involving the intramolecular disproportionation of the methyl groups as they approach one another, resulting from the deformation of the molecule, has been proposed:[48]

$$Me_2Cd \rightarrow CH_4 + Cd{:}CH_2 .$$

However, under the experimental conditions employed (150–200 mmHg, 212–327 °C), the role of the radical pathway should be considerable. This is indicated both by the poor reproducibility of the results, which can be accounted for by the uncontrolled change in the state of the vessel walls in the presence of impurities and by the increase of the yield of ethane with increasing temperature. The latter takes place as a consequence of the increase of the concentration of methyl radicals and the increase of the yield of their recombination product—ethane. Such findings are more likely to indicate a significant contribution of the free-radical pathways to the mechanism of the pyrolysis of

dimethylcadmium rather than the occurrence of an intramolecular rearrangement via the scheme presented by Heller and Taylor.[48]

A free-radical mechanism has been proposed[51] for the photolysis of dimethylcadmium, according to which the induced decomposition reaction

$$Me_2Cd + Me \rightarrow CH_4 + {}^{\cdot}CH_2CdMe$$

is the only source from which methane is formed.

It is believed that the mechanisms of the pyrolytic and photolytic decomposition of the majority of metal alkyls are the same. Thus a mechanism, equally probable for both pyrolysis and photolysis, has been proposed in a study[49] of the gas-phase decomposition of dimethylcadmium in a static system at a fixed initial reactant pressure of 150 mmHg and a temperature of 258 °C:

$$Me_2Cd \rightarrow Me + {}^{\cdot}CdMe \ ; \quad (11)$$

$$^{\cdot}CdMe \rightarrow Cd + Me \ ; \quad (12)$$

$$2Me \rightarrow C_2H_6 \ ; \quad (13)$$

$$Me + C_2H_6 \rightarrow CH_4 + Et \ ; \quad (14)$$

$$Me + Et \rightarrow C_3H_8 \ ; \quad (15)$$

$$Me + C_3H_8 \rightarrow CH_4 + Pr \ ; \quad (16)$$

$$Pr \rightarrow Me + C_3H_6 \text{ (polymerisation, etc.)} \quad (17)$$

It has been suggested that reaction (12) is faster than reaction (11) and that stages (13)–(16) have comparatively low activation energies and are rapid at the given temperature.

Features characteristic of the homogeneous–heterogeneous process have been observed in the pyrolysis of dimethylcadmium in a static system.[49] Extrapolation to $S/V = 0$ yielded the rate constant for the homogeneous dissociation of the first Cd–C bond: $k_{11} = 1.43 \times 10^{-5}$ s$^{-1}$ at 258 °C. The activation energy for this reaction, estimated as 43.5 ± 1.2 kcal mol$^{-1}$, has been identified with the dissociation energy of the first MeCd–Me bond. This value is close to $E_{11} = 45.8 \pm 1.0$ mol$^{-1}$, calculated[29] for the process in a stream of toluene. The dissociation energy of the second bond, calculated using thermochemical data, is $E_{12} = D_{12} = 21.4$ kcal mol$^{-1}$.[49]

When dimethylcadmium was pyrolysed in a stream of benzene,[50] a range of initial pressures was observed (80 to 163 mmHg) in which the rate constant was invariant, which corresponds to a first-order kinetic law; on the other hand, in the range of low initial pressures (10–20 mmHg), the rate constant increases with increasing pressure.[29] The mechanism of the decomposition of dimethylcadmium in toluene and benzene streams is analogous to that described above for the pyrolysis of zinc alkyls and includes, apart from the initiation stage, also reactions involving the abstraction of hydrogen from toluene and benzene by the methyl radical formed and subsequent recombination reactions of the benzyl and phenyl radicals. The kinetic and activation parameters for the individual stages of the above reaction have been published.[29,49,50] Activation energies in the range from 43.5 to 48.8 kcal mol$^{-1}$ and logarithms of the pre-exponential factor ranging from 11.9 to 13.4 have been obtained for reaction (11). The activation energy for reaction (12) has been estimated as 21.4 ± 4.0 kcal mol$^{-1}$.

The results of thermochemical studies, according to which the overall dissociation energy of the metal–carbon bonds in diethylcadmium is 52.9 ± 2 kcal mol$^{-1}$, suggest that diethylcadmium is thermally less stable than dimethyl cadmium.[1] The decomposition of gaseous diethylcadmium has been noted even at room temperature. However, detailed kinetic studies on the thermolysis of diethylcadmium and higher cadmium alkyls have not been made.

The kinetics of the deposition of metallic cadmium in the heterogeneous decomposition of gaseous diethylcadmium (temperature of the support 250–290 °C, temperature of the evaporator 19–50 °C) and di-isopentylcadmium (temperature of the support 240–250 °C, temperature of the evaporator 70–80 °C) have been investigated.[52] The amount of cadmium produced on the support depends on the temperature of the latter. The cadmium films obtained, with a thickness ranging from several microns to several tens of microns, constitute a light-coloured coating with a metallic lustre and satisfactory adhesion to the material of the support. The content of metallic cadmium in the coating is 99.5%. The microstructure and phase composition of the cadmium produced have been described.[46,47]

Solid dicylcohexylcadmium decomposes with liberation of metallic cadmium even at room temperature and for this reason the thermal decomposition has been studied in solution in benzene (100°, 30 h).[53] It was observed that the photodecomposition and thermal decomposition of dicyclohexylcadmium in benzene are accompanied by the formation of cyclohexane, cyclohexene, and bicyclohexyl.

A free-radical mechanism, in which the disproportionation of the radical formed predominates over the recombination and which is common to all metal alkyls, has been adopted for the pyrolysis of dicyclohexylcadmium [53] and di-isopentylcadmium [46] in solution and in the liquid phase in the absence of a solvent. It has also been suggested that the reaction involving the induced decomposition of the reactant via the abstraction of a hydrogen atom from the OMC molecule by the radical formed takes place. When solutions of diphenylcadmium in benzene are irradiated,[54] biphenyl and cadmium are formed preferentially, the contribution by the reaction with the solvent being small. On the other hand, the reaction involving the abstraction of hydrogen by the phenyl radical from the solvent molecule predominates in the photolysis of diphenylcadmium in dioxan.

## III. REACTIVITY AND STRUCTURE

Despite the fact that the experimental data for the kinetics of the pyrolysis of organozinc and organocadmium compounds refer solely to derivatives of lower alkyls, one can already reach certain conclusions about the reactivity of the above OMC in the decomposition reaction.

Under identical experimental conditions, the kinetic stability of the organometallic compounds formed is determined by the nature of the initial OMC, i.e. the nature of the metal atom and the radical. The kinetic stability of the lower alkyl and aryl compounds of zinc and cadmium varies in parallel with the variation of the average dissociation energy of the metal–radical bond ($\bar{D}$), although the initial step in the decomposition of the $MR_2$ molecules is their dissociation into R$^{\cdot}$ and $^{\cdot}$MR with the activation energy equal to the dissociation energy $D_1$. The second stage of the radical initiation reaction $^{\cdot}MR \rightarrow M + R^{\cdot}$ involving different compounds proceeds at different rates, as described above for zinc dialkyls. The dissociation energies of individual bonds and the average bond dissociation energies are listed in Table 3, from which it follows that, for the same metal, the energy of the abstraction of the first radical $D_1$ is greater than the energy of the abstraction of the second radical $D_2$ and the average dissociation energy of the metal–radical bond diminishes as the radical becomes more complex. The latter energy diminishes on passing from organozinc to organocadmium compounds.

With increase of the atomic number of the metal in Group IIB, the kinetic stability of the metal alkyls and metal aryls decreases, the thermal stability of the latter

being higher than that of the former.[1] The thermodynamic stability of the above OMC varies in the same sequence. It is known from thermochemical investigations that the average dissociation energy of the M–C bond for the OMC of transition elements within a single Group in Mendeleev's Periodic Table decreases with increase of the atomic number of the element.[55] For each individual element, the values of $\bar{D}$ can then be arranged in the following sequence:

$$M—Me > M—Et \cong M - n\text{-}Pr \cong M - n\text{-}Bu.$$

According to Voevodskii's rule,[60] the kinetic stability of the OMC decreases with increase of the thermodynamic stability of the radical liberated in the homolytic cleavage of the metal–radical bond. The ethyl derivatives of each metal are therefore less stable than its methyl derivatives. The thermal stability of the zinc alkyls decreases when the methyl group is replaced by the ethyl group to a lesser extent than for cadmium derivatives.

**Table 3.** The bond dissociation energies and the average metal–radical bond dissociation energies in metal alkyls (kcal mol$^{-1}$).

| $D_1$ | $D_2$ | $\bar{D}$ | Refs. |
|---|---|---|---|
| | Dimethylzinc | | |
| 47.0±2.0 | — | 43.1±0.5 | [56] |
| 47.2 | 35.0 | 41.1 | [28] |
| 47.2±1.0 | 36.8±3.0 | 42.0±1.5 | [57] |
| — | — | 41.0 | [58] |
| — | — | 42.7±2.2 | [55] |
| | Diethylzinc | | |
| — | — | 34.4 | [58] |
| — | — | 34.6±2.2 | [55] |
| 47.5 | 22.2 | 34.8 | [31] |
| | Di-n-propylzinc | | |
| — | — | 37.8±5.1 | [55] |
| | Di-n-butylzinc | | |
| — | — | 37.8±5.2 | [55] |
| | Dimethylcadmium | | |
| 45.8±1.0 | 21.0 | 33.4 | [29] |
| 44.7±2.0 | — | 35.2±0.5 | [56] |
| 45.8±1.0 | 20.8±2.0 | 33.3±1.0 | [57] |
| 43.5±1.2 | — | — | [59] |
| — | — | 32.9 | [58] |
| — | — | 34.4±1.6 | [55] |
| | Diethylcadmium | | |
| — | — | 26.5 | [58] |
| — | — | 26.4±1.6 | [55] |

The kinetic stability of organometallic compounds in the decomposition process can be estimated from the reaction rate constants measured under comparable conditions for the entire OMC reaction series. Depending on the decomposition conditions, the measured rate constant can be an effective quantity representing a combination of the rate constants for the elementary reactions or (for example, when the process is carried out in a stream of toluene) it is the true rate constant for the elementary stage limiting the rate of the overall decomposition. The rate-limiting stage is usually the elementary radical initiation reaction. Only in the latter case is the experimental rate constant for the elementary reaction in the free-radical non-chain process determined by the activation energy for this stage, since isotypical elementary reactions are then compared.[60]

However, there are no experimental data for such a comparison, because there have been no kinetic studies of the decomposition of series of compounds with successively altered structures. In certain cases the role of the steric effect can be significant.

The structure of the organometallic compound determines not only the dissociation energy of the metal–carbon bond but also the steric accessibility of the metal to possible attack in bimolecular collisions. It has been noted in a series of studies[61–63] that an increase of the degree of steric shielding of the metal atom in the OMC increases the kinetic stability of the latter. A method has been proposed[62,63] for the estimation of the degree of shielding of the reaction centre M in the OMC molecule by the organic group with the aid of the solid angles formed by the substituents at the metal on cylindrical projections of the OMC molecules. The degree of steric shielding of the reaction centre determines the effectiveness of the molecular collisions and can therefore serve as a criterion for the comparison of the contributions of the entropy term to the OMC decomposition rate constant. In order to eliminate the influence of electronic effects, the degree of shielding was estimated quantitatively and compared with experimental data for compounds with the same metal atom and with different substituents.[62,63] It was shown that the degree of steric shielding of the metal atom by the substituents is the dominant factor, which determines the kinetic stability of compounds of the type $MR_n$, where M = Hg or Cd.

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Thus it has been shown for lower zinc and cadmium alkyls and aryls that the mechanism of the thermal decomposition and photodecomposition varies with the decomposition conditions. At atmospheric and reduced pressures in a closed system and in a stream of the accompanying gas, the OMC investigated decompose via a free-radical mechanism, whilst under high vacuum conditions they decompose intramolecularly in an adsorption layer.

Although the general kinetic features of the thermal decomposition of the organozinc and organocadmium compounds as well as the kinetic and activation parameters of the radical initiation reaction in the homolytic cleavage of the first and second metal–carbon bonds have been established, systematic kinetic studies have not been made for an entire series embracing a large range of compounds with substituents of different lengths and with different degrees of branching. This limits to some extent the validity of the conclusions concerning the relation between the reactivity of the OMC considered, on the one hand, and their structure and the known thermodynamic characteristics of the dissociation of the given bond, on the other. The latter are represented in the literature only by the average metal–carbon bond dissociation energies and in certain cases the dissociation energies of specific ruptured bonds. On the other hand, there are so far no data on the average bond dissociation energies and enthalpies.

The causes of the self-inhibition of the decomposition of dimethylzinc have not so far been investigated. It is therefore important to study its decomposition under conditions which rule out self-inhibition. It is no less interesting to establish the order of the radical initiation reaction in the pyrolysis of diethylzinc in a closed system, which would help in determining the mechanism of the most difficult initial stage of the process investigated.

Complete quantitative analysis of the decomposition products for low degrees of reaction, which is essential for the determination of the detailed process mechanism and of

the role of the induced decomposition stage, has also not been carried out so far. Whereas the existence of the free-radical pathway to the decomposition of the zinc and cadmium OMC has been established unambiguously and gives rise to no doubts, additional studies are needed to solve the problem of the involvement of the intramolecular or intermolecular disproportionation reactions of the alkyl groups in the mechanism of the primary decomposition process.

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# The Energy Relations and the Nature of the Bond in Anhydrous Uranyl Compounds with Acido-ligands

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The energy relations governing the interaction of the uranyl ion with acido-ligands in a series of anhydrous crystalline uranyl complex salts are examined. Using the ideas concerning the electronegativity of the interacting species, the amount of ionic character of the bonds between $UO_2^{2+}$ and anions has been estimated (approximately 60-70%), which makes it possible to calculate the contribution of the electrostatic interaction to the crystal lattice energies of the anhydrous salts. It is shown that the stretching vibration frequencies of the uranyl ion in its complexes with acido-ligands are in no way correlated with the basicity and the electronegativity of the ions. The vibrational characteristics of the uranyl ion depend on many parameters (the structure of the complex, the symmetry of the molecule, the nature of the acido-ligand, the outer-sphere cation, etc.). The bibliography includes 72 references.

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## I. INTRODUCTION

The problem of the nature of the bonds in uranyl compounds still remains paramount in the chemistry of uranium. It is indissolubly linked with the understanding of the causes of the extremely high stability of the $UO_2^{2+}$ group in solutions and in the solid phase and also with the characteristics of its interaction with acido-ligands and neutral ligands. In view of the complexity of the problem as a whole, in the present review we shall consider only the bonding between the uranyl ion and acido-ligands in anhydrous crystalline salts.

Before proceeding to the direct estimation of the character of the bond between the uranyl ion and the acido-ligands, we shall deal briefly with the principal stages in the development of studies undertaken to understand the nature of the bonds in the uranyl group itself and the influence on the latter by equatorial ligands.

On the basis of the principle that the sum of the orders of the bonds formed by an atom in a compound is equal to the valence of the latter, Zachariasen[1] found that the multiplicity of the bonds in the uranyl group is less than two. Subsequently, in order to account for the high stability of the $UO_2^{2+}$ group, it was suggested[2,3] that the unshared electron pairs of the oxygen atoms are also involved in the reaction, which increases the multiplicity of the bonds in the OUO group. Later Vedovenko et al.,[4] who also used the valence principle, proposed a method for the estimation of bond orders somewhat different from that of Zachariasen,[1] based on the assumption that the sum of the bond orders is equal to the valence of only the central uranium atom. Here it was postulated that the bonds between uranium and the species surrounding it are covalent and that the charge on the uranium atom approaches zero ($^{+}O\equiv U\equiv O^{+}$). Equatorial ligands influence the bond strength in the OUO group in such a way that the enhancement of the electron-donating properties of the atoms entails the displacement of the unshared pairs and even of some of the valence electrons of the yl oxygen and a decrease of the uranium-oxygen bond order. Using the Pauling relation between the average bond strength $S$ and the valence of the ion, i.e. $S=V/N$, where $V$ is the valence and $N$ the coordination number, the strength of the bonds in the OUO group has been estimated[4-7] from the equation

$$R=R_1-\lg n, \qquad (1)$$

where $R$ is the length of a bond whose order is $n$ and $R_1$ the length of a bond whose order is unity and which amounts to 2.07 Å for a single bond in the $UO_3$ group. On the basis of the covalent model of the structure of uranyl compounds, a number of investigators[4-6] were able to explain a series of features of the spectroscopic properties of certain uranium(VI) coordination compounds.

The theory of the structure of uranyl compounds was developed further in the studies of Glebov,[8] who analysed in detail the possibilities of the principle in relation to uranyl compounds and showed that, for uranium(VI) coordination numbers of 6, 7, and 8, the ratio of the bond length and the bond strength is constant for almost all real uranium compounds. The following relation exists between $R_{UL}$ and $R_{UO}$:

$$R_{UL}^{N-2}=\langle R_N\rangle^N/R_0^2, \qquad (2)$$

where $\langle R_N\rangle$ is the geometrical mean of $R_{UL}$ and $R_{UO}$, which hardly changes in the series of compounds with identical coordination numbers.

At the same time the author showed[8,9] that, as a result of the endeavour to maintain the valence principle, the calculated bond orders in the uranyl group are not more than 1.5. In particular, Eqn.(1), which is satisfactorily applicable to uranates and uranium hydroxides and oxides, yields bond orders for uranyl complexes of less than 1.5. In addition, it has been noted[8] that a high multiplicity of the bonds, which entails a high degree of delocalisation of the bonding electrons of the uranyl group with a charge on the uranium atom close to zero, conflicts with structural data, according to which the equatorial ligands, including highly charged negative ligands, are disposed around the uranium atom, while in the $UO_2Cl_2$,[10] $UO_2SO_4$, $UO_2SeO_4$, $UO_2MoO_4$, $UO_2CrO_4$, and $UO_2WO_4$[12] structures the oxygen atom of the OUO group serves simultaneously as a ligand for a neighbouring layer. This presupposes a fairly high positive charge on the uranium atom and a negative charge on the oxygen atoms. The following distribution of charge in the uranyl group has been proposed: $^{-0.6}O-U^{3.2}-O^{-0.6}$,

and it has been suggested that it is in reality more ionic than would appear within the framework of the covalent model.

An anomalous dependence of the stretching vibration frequencies of the OUO group on the interatomic distances in it has also been observed.[8,9] For compounds with oxygen-containing ligands where $R_{UO}$ is in the range 1.65–1.80 Å, the stretching vibration frequencies of the bonds are smaller the shorter the bond. It has been noted that when a linear relation is maintained between the frequencies $\nu_{as}$ and $\nu_s$ of the $UO_2^{2+}$ group, the ratios between $K$ (the bond force constant, mdyn $A^{-1}$) for U–O and the distance $R_{UO}$, expressed by Badger's formula $R_{UO} = 1.08\,K^{-1/3} + 1.17$ and its various modifications ($K = 3.33 \times 10^{(2.07 - R_{UO})} - 0.73$; $R_{UO} = 1.993\,K^{-1/3} + 0.666$),[8] are inapplicable to the uranyl compounds indicated. This led the author[8] to divide all uranium(VI) compounds into two groups. Complexes with oxygen-containing ligands where the distances $R_{UO}$ in the OUO group do not exceed 1.8 Å were assigned to the first group. Compounds of the type of uranates and uranium hydroxides and oxides were assigned to the second group. It has been shown[8] that, in order to account for the observed anomalous behaviour of $\nu(UO_2^{2+})$ for uranyl coordination compounds, it is essential to take into account the contribution of the inner 6*p* and 6*s* shells to the formation of chemical bonds in the OUO group, which had been disregarded in earlier studies.

It was believed for a long time that only the 5*f*, 6*d*, and 7*s* electrons participate in the formation of the molecular orbitals of uranyl. A quasi-relativistic calculation[13] of the molecular orbitals of uranyl on the basis of the non-empirical version of LCAO-MO showed that inner 6*p* atomic orbitals interact actively with the orbitals of the oxygen atom and that their participation strengthens the bonds in the uranyl group. The inner 6*s* and 6*p* molecular orbitals ensure the presence of approximately 30% of the overall electron density in the uranyl group, which is probably equivalent to the existence of additional valence possibilities for the ions of actinide elements. It was established that a change in the distance $R_{UO}$ does not affect the populations of the outer 7*s*, 6*d*, and 5*f* orbitals of the uranium atom, altering only the electron population of the 6*p* orbitals. The latter are actively involved in the interaction with oxygen atoms for $R_{UO} \leq 1.8$ Å, whereas for longer interatomic distances ($R_{UO} \geq 1.8$ Å) the participation of the inner uranium shells in the formation of bonds is insignificant.

In the uranyl coordination compounds with $R_{UO} = 1.7$–$1.8$ Å the bonding in the OUO group is ensured by both the outer 6*d* orbitals of uranyls (the formation of $6d_\nu - 2s$ and $6d_\pi - 2p_\pi$ bonds with the oxygen atoms) and by the inner 6*p* orbitals of the uranium (the formation of bonds of the type $6p_\sigma - 2s$). The outer and inner MO of uranyl are then linked in such a way that the activation of the inner orbitals destabilises the outer MO.[8]

A complex relation is observed in the distribution of electron density. The independence of the charge density on uranium of the interatomic distance (within the limits 1.73–2.79 Å) conflicts with the traditional ideas, according to which the population of the AO diminishes with increase of the atomic distances, lowering the degree of covalence of the bonds in the OUO group and diminishing the shift of the electron density from the oxygen atoms to uranium.

In order to explain the dependence of the stretching vibration frequencies of the $UO_2$ group on $R_{UO}$, ideas concerning the shape and depth of the potential well for the OUO bonds in uranyl compounds have been used.[8,14] An increase of the depth and steepness of the potential well with decrease of the distance $R_{UO}$ corresponds to the normal relation between $\nu_{as}$ and $R_{UO}$, while the anomalous behaviour corresponds to an increase of the depth of the potential well accompanied by a decrease of its curvature.

Glebov[8,15] also attempted to take into account the influence of the ligand crystal field on the electronic structure of the uranyl group by carrying out calculations for clusters with six point charges in the equatorial plane of the uranyl group. The influence of the crystal field was characterised by a corresponding quantity, which represents the difference between the energies of the crystal field generated by the ligands on the uranium atom and on the uranyl oxygen atoms. These quantities were estimated from structural data, amounting to approximately 16–10 eV for uranates and to less than 8 eV for the coordination compounds. As a result, it was concluded that an increase of the crystal field of the equatorial ligands influences in the first place the electron populations of the outer AO of uranium, diminishing them. At the same time the populations of the inner AO of uranium change to a much lesser extent.

Thus Glebov[8,9,13–18] noted the principal contradictions arising in the interpretation of the characteristic features of the bonding in the OUO group within the framework of the covalent model and also outlined explanations of the anomalous properties of the compounds investigated. His conclusions refer predominantly to an isolated OUO group, which is virtually unperturbed by real ligands. The latter were taken into account only for oxygen-containing ligands, the class of halides as well as nitrogen-containing uranyl complexes being excluded from consideration. As before, questions associated with the constancy of the distances $R_{UO}$, which remain unaltered within the limits ~1.7–1.8 Å regardless of the coordination number of $UO_2^{2+}$ while the distances $R_{UL}$ change appreciably from one complex to another, remained unelucidated.

In discussing the bond strengths in uranyl complexes, it is necessary to take into account also the state of the substance to which they correspond. Indeed, analysis of the data for the interaction of the uranyl ion in aqueous solutions with acido-ligands such as $Br^-$, $Cl^-$, $NO_3^-$, and $SO_4^{2-}$ has shown that weak complexes are formed in this case. The logarithms of their stability constants ($\lg K_1$) are −0.3, −0.1, −0.3, and 1.9 respectively.[16–18]

## II. THE LATTICE ENERGIES OF COMPLEX URANYL SALTS

The concept of the lattice energy of the complex salts was introduced by Yatsimirskii[19] who regards it as the change in the internal energy of the substance of passing from the solid salt to the ionic gas consisting of the same ions as the crystal According to Yatsimirskii,[19] the lattice energy can be estimate from the equation

$$E_C = \Delta H_C^0 + \Delta H_A^0 - \Delta H_{CA}^0 \qquad (3)$$

where $\Delta H_C^0$, $\Delta H_A^0$, and $\Delta H_{CA}^0$ are the enthalpies of formation of the gaseous cation and anion and of the crystalline salt respec tively. Since Eqn.(3) is not related to either the nature of the ions or the nature of the forces acting between them, the lattice energies determined from it and referred to as experimental are evaluated from experimental thermodynamic data.

The heats of formation of certain anhydrous complex salts known at the present time as well as the heat of formation of the gaseous $UO_2^{2+}$ ion determined by Marcus[20] ($\Delta H_{f,298.15}^0 = 289.2 \pm 4.8$ kcal $mol^{-1}$) enabled us to calculate the crystal lattice energies for a series of anhydrous uranyl complexes. The heats of formation of the anions of certain uranyl salts are indicated in a handbook[21] and in a monograph.[19] The results of the calculation presented in Table 1 show that the lattice energies of the salts increase steadily on passing from uranyl perchlorate to the carbonate. Unfortunately, the list of complexes is limited to relatively simple uranyl salts, since there are no literature data for the heats of formation of complexes

of crystalline compounds and gaseous complexes of anions containing the uranyl group. In the absence of such data, the ionic lattice interaction energies can be calculated by means of the Kapustinskii equation,[22] which takes into account only the ionic charges and sizes:

$$E_C = 287.2 \cdot \frac{\Sigma_n Z_C Z_A}{r_C + r_A}\left(1 - \frac{0{,}345}{r_C + r_A}\right), \qquad (4)$$

where $\Sigma_n$ is the total number of cations and anions forming the molecule of the given salt, $Z_C$ and $Z_A$ are the formal ionic charges, and $r_C$ and $r_A$ are the ionic radii.

Table 1. The crystal lattice energies of uranyl compounds.

| Compound | $-\Delta H^0_{f,A(g)}$, kcal mol$^{-1}$ | $-\Delta H^0_{CA(c)}$, kcal mol$^{-1}$ | Refs. | $E^1_C$, kcal mol$^{-1}$ | $E^2_C$, kcal mol$^{-1}$ |
|---|---|---|---|---|---|
| $UO_2(ClO_4)_2$ | 91.5 | 302.5 | [21] | 408.7 | 416.3 |
| $UO_2Br_2$ | 59.9 | 271.8 | [24] | 443.2 | 460.2 |
| $UO_2Cl_2$ | 62.5 | 297.1 | [25] | 461.3 | 479.2 |
| $UO_2Cl_2$ | 62.5 | 300.0 | [26] | 464.2 | 479.2 |
| $UO_2(NO_3)_2$ | 80.0 | 330.8 | [20] | 460.0 | 468.9 |
| $UO_2(SCN)_2$ | 11.6 | 210.1 | [21] | 476.1 | 478.3 |
| $UO_2SO_4$ | 178 | 440.9 | [27] | 552.1 | 563.4 |
| $UO_2SO_4$ | 178 | 451.2 | [28] | 562.4 | 563.4 |
| $UO_2F_2$ | 66.9 | 397.9 | [29] | 553.3 | 551.4 |
| $UO_2F_2$ | 66.9 | 395.5 | [29] | 550.9 | 551.4 |
| $UO_2F_2$ | 66.9 | 394.7 | [30] | 550.1 | 551.4 |
| $UO_2(HCOO)_2$ | 107.1 | 447.1 | [31] | 521.1 | 511.4 |
| $UO_2(CH_3COO)_2$ | 122.0 | 467.9 | [29] | 513.1 | 509.9 |
| $UO_2(CH_3COO)_2$ | 122.0 | 476.1 | [32, 33] | 521.3 | 509.9 |
| $UO_2(OH)_2$ | 40.0 | 365.2 | [21] | 573.4 | 539.6 |
| $UO_2CO_3$ | 47 | 405.6 | [21] | 647.8 | 631.9 |

Notation: $-\Delta H^0_{f,A(g)}$ is the enthalpy of formation of gaseous anions, $-\Delta H^0_{CA(c)}$ the enthalpy of formation of the crystalline salt, and $E^1_C$ and $E^2_C$ are the lattice energies of the complex uranyl salts calculated from the Yatsimirskii and Kapustinskii equations respectively.

According to Marcus,[20] the radius of the uranyl ion is 1.40 Å. Table 1 also presents the results of the calculation of the lattice energies of the uranyl salts from Eqn.(4). Evidently the lattice energies calculated from the Kapustinskii equation, which takes into account only the electrostatic interactions between the ions, agree fairly well with the values obtained from thermal-chemical data.[3,4]

Yatsimirskii[23] believes that the interaction energy in a complex is determined in a general form by the equation

$$E_C = E_i + C + E, \qquad (5)$$

where $E_i$ is the energy of the interaction between the ions calculated from the Kapustinskii equation, $E$ the energy of extra-stabilisation by the crystal field, and $C$ the energy of formation of the covalent bond in the crystal.

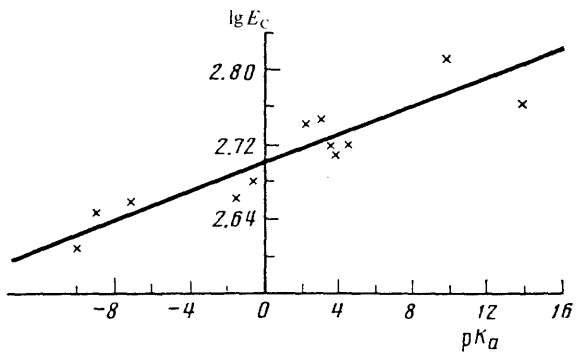
The covalent component of the bond between the cation and anion, arising as a result of partial charge transfer, is as a rule determined from the difference $\Delta E_{cov} = E_C - E_i$. For the salts considered, $\Delta E_{cov}$ does not exceed +20 kcal mol$^{-1}$. This value is probably determined not only by the nature of the bonds in the compounds investigated but also by the experimental errors in the determination of the heats of formation. Overall, it follows from Table 1 that the lattice energies found for the uranyl salts agree well with the values obtained from purely electrostatic considerations. At first sight it appears that, knowing the lattice energies, it is possible to estimate fairly readily the energies of the bonds between the uranyl ion and the acido-ligands in the anhydrous salts. However, in reality this is extremely difficult because the overall compositions of the salts say nothing about the way in which the ligands are bound and about the coordination number of the uranyl group. These compounds are formally coordination-saturated and they cannot be regarded as island structures. The coordination possibilities of the $UO_2^{2+}$ group in them are utilised by the formation of polymers. This is achieved both by binding the uranyl ions via bridging ligands ($Cl^-$, $SO_4^{2-}$, $C_2O_4^{2-}$, etc.) and as a result of the involvement in the coordination of the oxygen atoms of the OUO groups in neighbouring layers.

As an illustration, one may refer to the structural data for $UO_2Cl_2$ [10] and compounds of the type $UO_2EO_4$ (where E = S, Se, Cr, Mo, or W).[11,12] The coordination polyhedron of the uranium in these complexes is a pentagonal bipyramid, whose equatorial plane is formed by four bridging chlorine or oxygen atoms of the $EO_4^{2-}$ groups and the oxygen atom which plays a dual role. In the polymer structure the uranyl oxygen atom occupying the axial position in one polyhedron belongs to the plane of the pentagonal base of another polyhedron.

Table 2. Contributions of the electrostatic components of the U–L bonds to the crystal lattice energies of uranyl complexes.

| Compound | $R_{UL}$, Å × $m$* | $i_{UL}$ | $E_e$, kcal mol$^{-1}$ | $E_C$, kcal mol$^{-1}$ | $\Delta E_{cov}$, kcal mol$^{-1}$ |
|---|---|---|---|---|---|
| $UO_2Cl_2$ | 2.73×4 | 0.66 | 321.1 | 461.3 | 139.7 |
| $UO_2SO_4$ | 2.30–2.49 | 0.74 | 409.5 | 552.1 | 142.6 |
| $UO_2F_2$ | 2.43×6 | 0.74 | 606.6 | 553.3 | –53.3 |
| $UO_2CO_3$ | 2.50×4 (2.44×2) | 0.71 | 570.3 | 631.9 | 61.6 |
| $UO_2(OH)_2$ | 2.30×4 | 0.67 | 386.9 | 539.6 | 152.7 |

* Number of bonds.




Dependence of lg $E_C$ for uranyl salts on the basicity of the acido-ligand.[34]

Returning now to the crystal lattice energies of the anhydrous uranyl complexes (Tables 1 and 2), we may note that the sequence in which the lattice energies increase for the principal inorganic anions is fairly satisfactorily correlated with the variation of the basicities of the acido-ligands. The relation between lg $E_C$ and p$K_a$ shown in Fig.1, which has been treated by the method of least squares, can be described

by the following equation:

$$\lg E_C = 0.01 pK_a + 2,70. \quad (6)$$

Analysis of the thermodynamic quantities permits a number of conclusions. Firstly, the logarithms of the crystal lattice energies of the uranyl complexes vary linearly with the basicities of the acido-ligands. Secondly the $\lg E_C - pK_a$ relation can be used for a qualitative estimation of the lattice energies of anhydrous uranyl salts whose heats of formation are unknown. Finally, the calculation of the crystal lattice energies of the uranyl complexes, taking into account the electrostatic interaction only, indicates an appreciable amount of the ionic character of the bonds between $UO_2^{2+}$ and the acido-ligands in the crystalline uranyl complexes.

## III. ESTIMATION OF THE CONTRIBUTION OF THE ELECTROSTATIC INTERACTION OF $UO_2^{2+}$ WITH ACIDO-LIGANDS

The fact that the bonds between $UO_2^{2+}$ and acido-ligands are to a large extent electrostatic agrees with the classification of the uranyl cation as a hard Lewis acid.[35-37] In this connection it therefore becomes necessary to estimate quantitatively the amounts of ionic character of the bonds and the charges of the interacting ions. In order to estimate the electrostatic contribution, we employed the concept of electronegativity (EO), in which any bond is regarded as a superposition of covalent and ionic components.[38,39] Pauling, who introduced the concept of EO,[38] characterises electronegativity as the ability of an atom in a molecule (or in general in a chemical bond) to attract valence electrons. The EO theory was developed further in other investigations.[39-41,42-44] Sanderson[39-41] demonstrated the possibility of determining not only the effective charges and the coefficients of the ionic character and covalence but also the energies of the electrostatic and covalent bonding of the atoms in the molecule. For this purpose, one finds the geometrical mean of the EO on formation of the molecule and the EO of each atom is calculated relative to it. The bonding energies calculated for hundreds of organic and simple inorganic compounds differ from the experimental values by not more than 5%.

The application to uranyl compounds of the methods for the calculation of the effective atomic charges and of the amounts of ionic character of the bonds proposed by Sanderson[39-41] did not, however, yield reasonable results for the following reasons. In these calculations no account was taken of the coordination possibilities of uranium and they are hindered by the lack of data for the change in the electronegativity of uranium following the loss of an electron. In addition, and this is most significant, in the case of uranyl complexes with oxygen-containing ligands the oxygen atoms of the OUO group and of the anions are regarded as equivalent. The latter is probably valid only for a small number of compounds such as uranates in which the lengths of the bonds between the uranium atom and all the oxygen atoms surrounding it are comparable to the lengths of the uranium–oxygen bonds in the axial positions; the very concept of the uranyl group is abolished for such compounds.

It is preferable to use formulae for the calculation of the amounts of ionic character of bonds and effective charges proposed by Batsanov[42-44] for coordination crystals. The principal difference between the latter and molecules consists in the fact that the coordination number of an atom in such crystals is greater than its valence. The average "amount of ionic character of the bond" in the crystal is given by the following formula in the case of polyvalent atoms:

$$i_{cr} = \frac{Zi_{mol} + (K - Z)i_e}{K}, \quad (7)$$

where $Z$ is the valence of the atom, $K$ the coordination number, and $i_{mol}$ the amount of ionic character of the bond determined from the difference between the EO of the anion and the metal ($\Delta X$).[42,43] The covalent component is estimated from the polarity of the bonds between $UO_2^{2+}$ and the anions. The latter is determined by the competition between two factors—the attraction of electrons by the metal atom, which is proportional to its electronegativity $X_M$, and the ability of the metal to give up electrons to the anions, which is proportional to its ionisation potential $I_A$ in the valence state. The following relation has been proposed for the determination of the polarisation component of the bond, called the "electrostatic ionic character of the bond":[42-44]

$$i_e = \frac{I_A - X_M}{I_A + X_M}. \quad (8)$$

The degree of covalence of the bond is then calculated from the difference $1 - i_e$.

The EO have been published[42-44] for acido-ligands ($NO_3^-$, $ClO_4^-$, $SO_4^{2-}$, etc.) taking into account the interactions within the corresponding group. The knowledge of $i_{cr}$ makes it possible to calculate the effective atomic charges $Z^*$, which characterise the distribution of electron density in the region of the chemical bond:

$$Z^* = Z - K(1 - i_{cr}). \quad (9)$$

The quantity in brackets corresponds to the degree of covalence of the bond, since the overall contribution of all the interactions is assumed to be unity.

The electronegativity of the uranyl ion $UO_2^{2+}$ was assumed to be 1.38.[45] Its estimation from the formulae proposed by Zhang[46] and Allred[47] leads to approximately the same value. The ionisation potentials of anions were given in a handbook[48] and in another publication.[49] In the calculation the uranyl group was regarded as a bivalent point cation in which the interaction of the uranium and oxygen atoms is disregarded. The quantity $i_{mol}$ was determined from tabulated data on the basis of the relation between the amount of ionic character of the bonds and $\Delta X$.[42,43]

The calculations showed that the amounts of ionic character of the bonds between $UO_2^{2+}$ and the anions are mainly in the range 60–70% for all the anhydrous solid complexes. The increase of the coordination number (C.N.) from four to six is not then unduly reflected in the change of the amount of ionic character of the bond, since the effective charge $Z^*_{eff}$ is very significantly reduced. Naturally the concept of the effective charge on the uranyl ion is fairly arbitrary; it reflects in only a simplified form the distribution of charges in the case where the uranyl ion is regarded as a doubly charged cation.

Like the effective charges, the amounts of ionic character of the bonds do not exhibit an explicit dependence on the nucleophilicity of the anions, although, overall, a definite tendency towards a decrease of the amounts of ionic character of the bonds between the uranyl ion and the equatorial ligands can be traced as the basicity of the ligands increases. The closeness of the amounts of ionic character of the bonds between $UO_2^{2+}$ and the acido-ligands in different uranyl compounds can serve as evidence that the mechanism of the interaction of these species is predominantly electrostatic and confirms the assignment of the uranyl[35-37] to hard Lewis acids.

Using the ideas developed by Batsanov[44] for mixed three-centre systems $A_1–M–A_2$ or $M_1–A–M_2$, it is possible to put forward certain considerations concerning the character of the bonding in the uranyl group in complexes having the general formula $UO_2X_n$. According to the Pauling principle, which requires a constant population of the metal orbitals and

the possibility of saturating the EO, an increase in the amount of ionic character of the $A_1$–M bond (or the $M_1$–A) bond should be accompanied by an increase of the degree of covalence of the M–$A_2$ (or A–$M_2$) bond. This is usually expressed by a change in the lengths of the corresponding bonds and their vibration frequencies in such a way that the greater ionic character of one of these bonds entails a greater covalent character of the other. Since the structure of uranyl compounds is such that the oxygen atoms of the OUO group are in the *trans*-positions with respect to the equatorial ligands, an increase of the amount of ionic character of the UO–L bond should probably tend to increase the degree of covalence of the U–O bonds. Indeed, analysis[50] of structural data for uranyl complexes having coordination numbers of 4, 5, and 6 shows unambiguously that the greater the $R_{UL}$, the smaller the $R_{UO}$.

In the series of isostructural anhydrous uranyl compounds $UO_2MoO_4$, $UO_2SeO_4$, $UO_2SO_4$,[11,12] and $UO_2Cl_2$,[10] in which the uranium polyhedron is a pentagonal pyramid, an increase of $R_{UL}$ (2.30–2.35, 2.30–2.49, 2.30–2.54, and 2.52–2.73 respectively) is accompanied by a shortening of the $R_{UO}$ distances (1.76 and 1.81, 1.78 and 1.79, 1.73 and 1.80, and 1.73 and 1.78 Å). This is equivalent to an increase of the degree of covalence of the uranium–oxygen bonds in the OUO with increase of the amount of ionic character of the bonds with the acido-ligands. The high degree of covalence of the bonds in the OUO group and the electrostatic character of the interaction with the acido-ligand are in good agreement with the autonomous chemical behaviour of $UO_2^{2+}$ and the constancy of the bond length $R_{UO}$ in the range 1.65–1.80 Å regardless of the nature of the ligand and the coordination number.

In contrast to *d*-block elements, the geometry of the coordination sphere of uranyl is apparently determined mainly by electrostatic and steric factors and not by the degree of overlap of the uranyl and ligand orbitals. This agrees with the absence of a correlation between $R_{UO}$ and $R_{UL}$, on the one hand, and the ligand crystal field energies, estimated by Glebov,[15] on the other. The high strengths of the bonds in the crystalline complexes of uranyl with ligands which give rise to the weakest complexes in solution ($ClO_4^-$, $Cl^-$, $NO_3^-$, and $SO_4^{2-}$) can be readily accounted for on the basis of the concept of the electrostatic character of the interaction of $UO_2^{2+}$ with acido-ligands. This is indicated by the high crystal lattice energies of uranyl sulphate, fluoride, carbonate, and nitrate (Table 1) calculated from thermodynamic data. The increase in the stability of the compounds of the above most electronegative anions in the crystalline state is probably achieved as a result of the formation of extremely strong electrostatic bonds with the acido-ligands.

On the other hand, the idea of a large amount of ionic character of the bonds between $UO_2^{2+}$ and equatorial ligands, especially the most electronegative of these, makes it possible to understand the tendency of these bonds to ionise in solution and hence their weak capacity for complex formation.

The electrostatic nature of the bonding between $UO_2^{2+}$ and the ligands agrees well with the known facts indicating the preferential interaction of the above cation with hard bases containing oxygen or halogen atoms. Under the usual conditions, the uranyl ion does not form bonds with soft bases containing nitrogen, sulphur, and phosphorus electron-donating atoms. Such reactions become possible only in a series of organic solvents exhibiting a much smaller solvating effect and polarising capacity than water.

The estimated amounts of ionic character of the bonds in the uranyl compounds can be used to calculate the electrostatic contributions to the crystal lattice energies $E_{lat}$ with the aid of the equation proposed by Sanderson,[39–41] in which $E_{lat}$ is regarded as the sum of the electrostatic ($E_e$) and covalent ($E_{cov}$) contributions:

$$E_{lat} = t_e E_e + t_c E_{cov},$$

where $t_e$ and $t_c$ are respectively the coefficients of the ionic character and covalence of the bonds, whose sum is unity.

The electrostatic interaction energy is

$$E_e = t_e \times 332 e^2/R_0,$$

where $R_0$ is the bond length and 332 is a coefficient which makes it possible to express the bond energy in kcal $mol^{-1}$.

The covalent contribution is calculated as the geometrical mean of the energies of two homeopolar bonds.[39–41] We calculated[53] the electrostatic contributions $E_e$ to the crystal lattice energies for a series of uranyl salts with known structures (Table 2). In the calculation of $E_e$, the amounts of ionic character of the bonds $i_{UL}$ calculated by ourselves were adopted as the $t_e$. For $UO_2SO_4$ with different U–ligand bond lengths, their values were either averaged or the length of each bond was taken into account. Comparison of the $E_e$ with the crystal lattice energies of the uranyl salts showed that the electrostatic interactions make the main contribution to the crystal lattice energy.

The overall contribution of the covalent interaction energy and the energy of the extra-stabilisation by the crystal field can be estimated from the difference $\Delta E_{cov} = E_c - E_e$, because, according to Yatsimirskii,[23] the energy of the interaction in the complex is determined in the general form by Eqn.(5). It follows from Table 2 that $\Delta E_{cov}$ is much smaller than $E_e$; it is negative only for uranyl fluoride, which is probably associated with errors in the determination of the $UO_2F_2$ structure;[51] the structure has been discussed by Ohwada.[52] It is known[53] that this structure is atypical for uranyl halides, which have a characteristic coordination number of five.

## IV. ANALYSIS OF THE VIBRATION FREQUENCIES OF THE $UO_2^{2+}$ ION IN ITS COMPLEXES WITH ACIDO-LIGANDS

In connection with the problem of the interrelation between the structure and properties of a substance (in particular spectroscopic properties), the determination of various correlations between the above characteristics is always regarded as important. Different views on this problem are held as regards uranyl compounds. It has been noted[35] that several spectrochemical series, differing in the sequence of the ligands, have been proposed for uranyl coordination compounds. Having applied the *d*-element spectrochemical series to uranyl compounds, McGlynn et al.[54] assumed that the stretching vibration frequencies $\nu_s$ and $\nu_{as}$ of the $UO_2^{2+}$ ion decrease as a function of the nature of the ligands in the following sequence: $NO_3^- > F^- > H_2O >$ Phen ≅ Py $> NO_2^- > NCS^- > NH_3 >$ ethylenediamine $> CN^-$. The dependence of the state of the bonds in the $UO_2^{2+}$ group on the nature of the ligands in uranyl complexes has been postulated by Dyatkina and Mikhailov.[3] These ideas were developed further in a study[4] whose authors concluded that the orders of the uranyl and equatorial bonds are inter-related and that the uranyl vibration frequencies are extremely sensitive to changes in bond orders and the corresponding force constants. The bond orders have been estimated for a series of compounds, including uranates and uranium oxides, and the frequencies $\nu_s$ and $\nu_{as}$ for $UO_2^{2+}$ and the force constants have been compared. A dependence of the bond orders in the uranyl complexes on the nature of not only the ligands but also the outer-sphere cation has been noted.[56]

At the same time, there have been studies in which the absence of correlations between the vibration frequencies of uranyl and the nature of the ligands has been pointed out.

Having analysed complexes analogous to those investigated by McGlynn et al.,[54] Bullock[57] concluded that the series of frequencies estimated by McGlynn et al.[54] are erroneous. Volod'ko et al.[55] claim that the variation of the vibration frequencies of $UO_2^{2+}$ in different compounds is not correlated with the position of the ligands in the spectrochemical series.

The absence of such correlations has also been noted by Day and Venanzi,[58] who regard the variation of the uranyl vibration frequencies as a result of the superposition of vibrational and electronic interactions. The former are determined by the vibration of the bonds between the uranium atom and the equatorial ligands, the intensity of these vibrations depending on the force constants of the system (including the metal–ligand bonds) and on the mass of the ligands. The electronic interaction arises as a consequence of electron transfer to the uranyl ion and is determined by the electron-donating capacity of the ligand. It is to be expected that the $UO_2^{2+}$ vibration frequencies should decrease with increase of the electron-donating capacity. However, the superposition of the above two factors makes the changes in the vibration frequencies of the uranyl ion unpredictable. Bagnall and Wakerley,[59] who analysed 18 uranyl complexes, hold the same view.

Examination of the electronic spectra and the EO of uranyl compounds with various ligands led to the conclusion[60] that both the positions and intensities of the electronic transition bands are independent of the chemical nature of the ligands and are determined solely by the geometrical structures of the first coordination sphere of the uranium atom. The influence of the ligands can be taken into account only when the symmetries of the inner coordination sphere of uranium are identical.

A similar conclusion follows also from the theoretical analysis of the absorption spectra of uranyl complexes.[61–64] The change in the mass of the ligand from 10 to 200 a.u. in the complexes $UO_2X_n$ (where $n$ = 4, 5, 6), for an unchanged internal force field of the uranyl group and when the remaining parameters such as the mass of the atom X, the lengths of the UX bonds, and their force constants are varied within specified limits, alters the frequencies $\nu_S$ of the $UO_2^{2+}$ group by only 5 $cm^{-1}$, while the frequencies $\nu_{as}$ remain virtually constant. The frequencies $\nu_S$ and $\nu_{as}$ are also independent of the uranium–ligand bond length in the range 1.8–2.8 Å. The variation of the force field of the ligands within wide limits can alter the $UO_2^{2+}$ vibration frequencies by not more than ~10 $cm^{-1}$ in complexes with $D_{4h}$ symmetry, by ~13 $cm^{-1}$ for the $D_{5h}$ symmetry, and by ~15 $cm^{-1}$ for the $D_{6h}$ symmetry. It has also been shown for halide complexes having the general formula $M_2[UO_2X_4]$ that the frequencies $\nu_{as}$ hardly change on replacement of any number of chlorine atoms by bromine atoms regardless of the symmetry of the complex anion associated with the same cation.[63,64] The force constants of the U–O bonds in these compounds are similar and amount to 6.6 to 6.8 mdyn $A^{-1}$.

The list of investigations in which the influence of ligands on the force constants and vibration frequencies of the bonds in uranyl compounds has been discussed may be greatly expanded, since we have mentioned only some of them. We may note that in the studies quoted, with the exception of Refs.61–64, both complexes containing only acido-ligands (which consist of anions) and compounds with a mixed type of coordination sphere, containing acido-ligands and neutral ligands, were considered simultaneously. Such complexes should probably be discussed separately in order to eliminate the superposition of the two factors indicated when general relations are deduced.

In the present review we shall consider the behaviour of $\nu_{as}$ for the $UO_2^{2+}$ group in uranyl complexes containing only acido-ligands, starting with anhydrous salts (Table 3). The study of the vibrational spectra of the latter is a fairly complex task not only because of the difficulty of synthesising these compounds but also because they are extremely hygroscopic. This factor has been frequently noted by various authors; in particular, we have demonstrated this for the anhydrous compounds $UO_2Cl_2$ [65] and $UO_2(NO_3)_2$,[66] whose infrared spectra changed very markedly after an extremely brief contact of the specimen with air. Thus, apart from the three intense absorption bands at 950, 835, and 775 $cm^{-1}$, a series of additional intense bands appeared in the $UO_2Cl_2$ spectrum in the range 950–900 $cm^{-1}$. The same situation probably obtains also for $UO_2(ClO_4)_2$, $UO_2F_2$, and $UO_2Br_2$, whose spectra are not only characterised, according to the data of different workers, by different frequencies $\nu_{as}$ ($UO_2^{2+}$) but also differ as regards the number of absorption bands[64] (Table 3).

**Table 3.** The vibration frequencies $\nu_{as}$ of the $UO_2^{2+}$ group in the spectra of uranyl complexes.

| Compound | $\nu_{as}$, $cm^{-1}$ | Refs. | Compound | $\nu_{as}$, $cm^{-1}$ | Refs. |
|---|---|---|---|---|---|
| $UO_2(ClO_4)_2$ | 996,965,961 | [64] | $Cs_2[UO_2Br_4]$ | 925,920 | [64] |
| $UO_2(ClO_4)_2$ | 965 | [5] | $(PyH)_2[UO_2Br_4]$ | 935 | [64] |
| $UO_2Br_2$ | 945,905 | [64] | $Li_2[UO_2Cl_4]$ | 940 | [64] |
| $UO_2Cl_2$ | 950 | [65] | $Na_2[UO_2Cl_4]$ | 935 | [64] |
| $UO_2Cl_2$ | 990,980,965 | [66] | $K_2[UO_2Cl_4]$ | 925 | [64] |
| $UO_2Cl_2$ | 977 | [67] | $Rb_2[UO_2Cl_4]$ | 920 | [64] |
| $UO_2SO_4$ | 930 | [68] | $Cs_2[UO_2Cl_4]$ | 920 | [64] |
| $UO_2CrO_4$ | 930 | [68] | $(PyH)_2[UO_2Cl_4]$ | 924,914 | [64] |
| $UO_2MoO_4$ | 932 | [68] | $NO[UO_2(NO_3)_3]$ | 940 | [66] |
| $UO_2WO_4$ | 936 | [68] | $NH_4[UO_2(NO_3)_3]$ | 952 | [57] |
| $UO_2F_2$ | 1000 | [52] | $K[UO_2(NO_3)_3]$ | 960 | [57] |
| $UO_2F_2$ | 1040,927,923 | [64] | $Rb[UO_2(NO_3)_3]$ | 955 | [57] |
| $UO_2(CH_3COO)_2$ | 950 | [64] | $Cs[UO_2(NO_3)_3]$ | 956 | [57] |
| $UO_2(CH_3COO)_2$ | 942 | [69] | $(NH_4)_2[UO_2(NO_3)_4]$ | 960 | [55] |
| $UO_2CO_3$ | 930 | [64] | $Rb_2[UO_2(NO_3)_4]$ | 945 | [55] |
| $UO_2CO_3$ | 965 | [4] | $(NH_4)_3[UO_2F_5]$ | 885,877 | [70] |
| $\beta$-$UO_2(OH)_2$ | 892 | [9] | $K_3[UO_2F_5]$ | 870 | [70] |
| $\gamma$-$UO_2(OH)_2$ | 890 | [9] | $Rb_3[UO_2F_5]$ | 860 | [70] |
| | | | $Cs_3[UO_2F_5]$ | 850 | [70] |
| | | | $K_5[(UO_2)_2F_9]$ | 870,858 | [55] |
| | | | $Na[UO_2(CH_3COO)_3]$ | 931 | [55] |
| | | | $Rb[UO_2(CH_3COO)_3]$ | 924 | [55] |
| | | | $Cs[UO_2(CH_3COO)_3]$ | 920 | [55] |
| | | | $(NH_4)_4[UO_2(CO_3)_3]$ | 888 | [55] |
| | | | $Na_4[UO_2(CO_3)_3]$ | 876 | [64] |
| | | | $K_4[UO_2(CO_3)_3]$ | 881 | [55] |
| | | | $Rb_4[UO_2(CO_3)_3]$ | 877 | [55] |
| | | | $Cs_4[UO_2(CO_3)_3]$ | 877 | [55] |
| | | | $K_2[UO_2(CO_3)_2]$ | 856 | [55] |

Analysis of the vibration frequencies in the infrared spectra of anhydrous uranyl salts has shown that they exhibit no correlations with the basicities of the ligands; this is indicated by the data in Table 3, where the compounds are arranged in order of increasing $pK_a$ of the ligands. Nor are there any correlations with the electronegativities of the anions. It is striking that the highest frequencies $\nu_{as}$ ($UO_2^{2+}$) correspond to anions with the highest EO ($F^-$, $ClO_4^-$, and $NO_3^-$). On the other hand, complexes with other anions, which also have high EO ($SO_4^{2-}$ and $CO_3^{2-}$), have frequencies $\nu_{as}$ close to the vibration frequencies of compounds with less electronegative anions ($Br^-$ and $CH_3COO^-$). Without ruling out the possibility of an inadequate reliability of the experimental vibration frequencies of certain anhydrous salts, the difficulties in determination of which were noted above, one can postulate that the above inconsistencies are determined also by the difference between the structures of the anhydrous uranyl salts. Table 3 also lists the frequencies $\nu_{as}$ ($UO_2^{2+}$) in the spectra of compounds with more complex compositions, incorporating a complex anion and outer-sphere cations. Analysis of the changes in the $\nu_{as}$($UO_2^{2+}$) listed in Table 4 following the replacement of the

ligand indicates the absence of a correlation between $\nu_{as}$ and the basicity of the acido-ligand. On the other hand, in the series of isostructural hexacoordinate uranyl complexes, containing bidentate acido-ligands, the transition from trinitrato- to triacetato- and tricarbonato-uranylates reveals a tendency towards a decrease of $\nu_{as}$ with increase of the basicities of the anions. However, the data for these three compounds are clearly insufficient to infer the existence of this type of general relation.

**Table 4.** The vibration frequencies $\nu_{as}$ of the $UO_2^{2+}$ group in the spectra of anionic uranyl complexes with $Rb^+$ as the outer-sphere cation.

| Compound | $pK_a$ | $X$ (Ref. 24) | $\nu_{as}$, $cm^{-1}$ | Refs. |
|---|---|---|---|---|
| $Rb_3[UO_2Cl_5]$ | ~7 | 3.2 | 920 | [64] |
| $Rb[UO_2(NO_3)_3]$ | ~1.4 | 3.8 | 955 | [57] |
| $Rb_2[UO_2(NO_3)_4]$ | ~1.4 | 3.8 | 945 | [55] |
| $Rb_3[UO_2F_5]$ | 3 | 4.0 | 860 | [70] |
| $Rb[UO_2(Cl_3COO)_3]$ | 4.7 | 3.0 | 924 | [55] |
| $Rb_4[UO_2(CO_3)_3]$ | 10.2 | 3.6 | 877 | [55] |

Note. The $pK_a$ and the electronegativities $X$ for the anion are quoted.

The analysis of the variation of the frequency $\nu_{as}(UO_2^{2+})$ under the influence of the outer-sphere cation is also of interest. It is known that there is competition in uranyl complexes between the uranyl ion and the outer-sphere cation: both withdraw electron density from the anion in the three-centre system U–A–M. The results of studies on chloride complexes were previously discussed by Vdovenko.[71] The data in Table 3 show that, in the series of isostructural tetrachloro- and pentafluoro-uranylates, the transition from $Li^+$ and $Cs^+$ entails a monotonic increase of the frequency $\nu_{as}(UO_2^{2+})$. From the standpoint of the theory of electronegativity, the EO of the outer-sphere cations diminishes on passing from $Li^+$ to $Cs^+$ (EO is 1.1 for $Li^+$, 0.9 for $Na^+$, 0.8 for $Rb^+$, and 0.7 for $Cs^+$).[42] Since the EO of the $UO_2^{2+}$ group is 1.38,[45] i.e. is greater in absolute magnitude than the EO of metal ions, the electron density shifts from the anion to the uranyl ion, which means that the M–A bond is more electrostatic than the U–A bond and the amount of ionic character of the M–A bonds is greater the lower the EO of the outer-sphere cation. With increase of the amount of ionic character of the M–A bonds, there is a corresponding increase of the degree of covalence of the U–A bonds. The increase of the degree of covalence of the uranium–ligand bonds should induce a decrease of the frequency $\nu_{as}$ of the uranyl ion, which has in fact been observed for the halide complexes.

In the case of complex polyatomic polyfunctional anions, this type of relation breaks down. Table 4 shows that the frequencies $\nu_{as}$ in the spectra of uranyl nitrates and carbonates are almost insensitive to the effects of the outer-sphere cation.[72] However, this not only does not conflict with the effects discussed above but actually confirms them. Indeed, the electron density shifts from the oxygen atoms of the anions in such complexes and is distributed between the uranium atom and the central atom of the acido-ligand (such as the carbon atom in $CO_3^{2-}$ or the nitrogen atom in $NO_3^-$) and not between the uranyl ion and the outer-sphere cation. As a consequence of this, the influence of the outer-sphere cation is hardly reflected in the vibration frequencies of the $UO_2^{2+}$ ion.

The above analysis of the vibration frequencies of the $UO_2^{2+}$ ion in its complexes with acido-ligands shows that, for the series of compounds indicated, the dependence of $\nu$ on the nature of the anions and in particular on their basicity is limited and cannot be regarded in isolation from the characteristics of specific structures. When the complexes contain neutral ligands, the situation probably becomes still more complex. A multiplicity of various structures of uranyl complexes having coordination numbers of 4, 5, and 6 are known; on passing from one compound to another, there is as a rule a change in not just one but immediately in a whole series of parameters characterising these structures. It is therefore almost impossible to relate the changes in the vibration frequencies of the $UO_2^{2+}$ group solely to any one of them.

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Thus one may conclude that the energy relations governing the interaction of the uranyl group with acido-ligands in anhydrous complexes are described fairly accurately in terms of electrostatic ideas. This justifies the hypothesis that the above approach to the description of the interaction between the components of the complex is legitimate also in uranyl compounds having a more complex composition.

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# Stable Radicals and the Kinetics of the Radical Polymerisation of Vinyl Monomers

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The literature data and the results of studies by the authors of the review on the kinetics and mechanism of the radical polymerisation of vinyl monomers in the presence of stable radicals of different classes are treated systematically and discussed. The principal kinetic features associated with the influence of the structure of the monomer and the stable radical, the type of initiation, and the nature of the initiator on the polymerisation inhibited by stable radicals are noted. Equations are presented for the calculation of the kinetic parameters of the principal elementary reactions responsible for the initiating and inhibiting effect of stable radicals.
The bibliography includes 155 references.

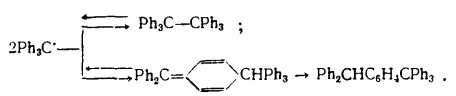
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The mechanism of the polymerisation of vinyl monomers has been studied in fair detail and numerous reviews and books, for example, Refs.1–4, have been devoted to this problem. The free-radical polymerisation inhibitors have aroused much interest in recent years.

## I. HYDROCARBON RADICALS

Gomberg, who synthesised hexaphenylethane,[5] believed it to be the pure triphenylmethyl radical and it was only later established, in 1909, that "Gomberg's radical" is a dimer in thermodynamic equilibrium with the triphenylmethyl radical. For example, in benzene solution at room temperature only about 2% of the dimer is dissociated into free radicals.[6] It is of interest that an extremely stable hydrocarbon with a melting point of 234 °C has been found among triphenylmethyl dimers:



The triphenylmethyl radical inhibits the thermal polymerisation of styrene.[7] As expected, the measured induction period of the polymerisation reaction proved to be much shorter than the value calculated from the consumption of the inhibitor:[3]

$$\tau = \mu \frac{[X]}{W_i} \quad ,$$

where $W_i$ is the rate of initiation, [X] the initial inhibitor concentration and $\mu$ the stoichiometric inhibition coefficient equal to the number of reaction chains broken by one inhibitor species.

Hexaphenylethane dissolved in styrene served as the source of radicals in the above investigation.[7] According to the authors' data, the rupture of one reaction chain requires 77 hexaphenylethane molecules, which corresponds to $\mu = 0.013$, in good agreement with the data of Theilacker and Ewald.[6]

In the presence of benzyl and diphenylmethyl radicals, which are more reactive than the triphenylmethyl radicals, the polymerisation of acrylonitrile and methyl methacrylate has no induction period and its rate is comparable to the rate of the initiated reaction.[8,9]

## II. HYDRAZYL RADICALS

Numerous studies have been devoted to the influence of the stable 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical[10] on the rate of polymerisation of vinyl monomers. The high stability and relative availability of DPPH made it possible to employ this stable radical in the study of the photolysis and radiolysis of various compounds, cage effects, and the decomposition of initiators.[11–15]

DPPH is an effective inhibitor of the polymerisation of styne and vinyl acetate.[16–19] With increase of the DPPH concentration, the induction period shortens, which is caused, according to the authors, by the additional initiation due to the stable radical. It follows from the analysis of the dependence of $\tau$ on the initiator concentration [DPPH] that approximately 10% of the initial amount of the DPPH is consumed in chain initiation. However, one should note that the amount of the hydrazyl radical consumed in the initiation of the reaction is determined by the nature of the monomer. At the end of the inhibition period the steady-state rate of polymerisation falls. The bifunctionality of DPPH (weak initiation and strong inhibition) has also been noted in the polymerisation of styrene.[20]

Despite the above experimental facts and on the basis of the high activity of DPPH in relation to the growing chain alone, Matheson, Bartlett, and co-workers believe that it is possible to use this radical for the determination of the kinetic characteristics of the polymerisation—the rate of chain initiation and the ratio of the rate constants for chain propagation and termination $k_p/k_t^{1/2}$. It is then assumed that one radical terminates only one kinetic chain.

The mechanism proposed earlier[21,22] for the interaction of DPPH with active free radicals R$^\cdot$ consisted in the addition of R$^\cdot$ in the *para*-position in one of the phenyl groups. Further investigations showed that DPPH reacts to form a complex mixture of products: biphenyl, diphenylamine, 1-(4-cyanoisopropylphenyl)-1-phenyl-2-picrylhydrazine, and small amounts of $\alpha\alpha'$-diphenyl-2-picrylhydrazine.[23,24] If the reaction is propagated in the presence of oxygen, then

the interaction of peroxy-radicals with DPPH complicates the mechanism still further.[25-27]

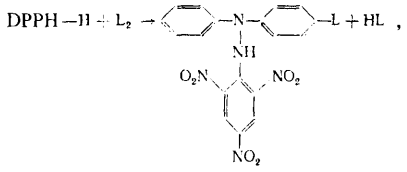
The possibility of the interaction of one DPPH species with several free radicals was first demonstrated experimentally by Hammond et al.[28] in a study of the decomposition of αα'-azobisisobutyronitrile (AIBN). It was assumed that the destruction of the cyanoisopropyl radicals with participation of DPPH is accompanied by the regeneration of the latter:

$$(CH_3)_2\dot{C}CN + DPPH \rightarrow CH_2{=}C(CH_3)CN + H{-}DPPH;$$
$$H{-}DPPH - (CH_3)_2\dot{C}CN \rightarrow (CH_3)_2CHCN + DPPH.$$

The complexity of the interaction of DPPH with free radicals was also confirmed by the result of the determination of the initiation efficiency factor $f$ for AIBN.[22] Its values proved to be appreciably lower than those obtained by other workers using independent methods.

DPPH reacts with inorganic and organic acids via an ionic mechanism:[29]

$$DPPH + L^- \rightleftarrows [DPPH{-}L]^-,$$
$$[DPPH{-}L]^- + H^+ \rightarrow DPPH{-}H + {}^1/_2L_2,$$



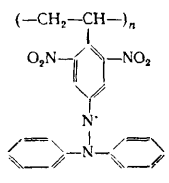
where $L^-$ is the anion. It follows from the data presented that the inhibition of polymerisation processes by DPPH cannot be regarded as proof of the radical character of the reaction.

By measuring the DPPH concentration spectrophotometrically, Bengough[30] observed that the induction period in the polymerisation of vinyl acetate is not the same as the time required for the complete disappearance of the stable radical from the reaction system. This is apparently associated with the fact that the stoichiometric inhibition coefficient is not unity.

Analogous results were obtained also in the study of the thermal polymerisation of styrene inhibited by DPPH.[31] The rate of formation of active radicals, found from the time variation of the absorption intensity ($\lambda$ = 525 nm), proved to be seven times greater than the value calculated from the equation relating the induction period to the initial concentration of the stable radical. This difference between the rates of initiation is caused not only by the stoichiometry of the inhibition but also by the characteristics of the mechanism of the thermal initiation[32,33] and the possibility of the decomposition of DPPH by UV radiation.[24]

The limits of the applicability of DPPH in the study of the kinetics of the decomposition of certain compounds and in the determination of their initiating activity have been analysed[34] and it has been shown that acceptable results are obtained only for the ratio [DPPH]/[I] ≤ 0.5.

Multiradical inhibitors based on DPPH, of the type[35,36]



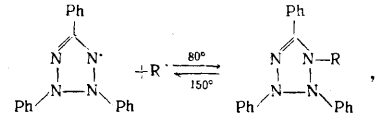
are of definite interest.

It follows from the literature data[16-38] that, when DPPH is used as the source of radicals, it is essential to know and take into account the chemical side reactions. Some investigators explained the decrease of the steady-state rate of polymerisation in the presence of DPPH (secondary inhibition) as the influence of the products of the primary inhibition responsible for the induction period.[37] The retardation of the reaction is usually attributed to the presence of nitro-groups. In order to test this hypothesis, 2-(2,6-dinitrophenyl)-1,1-diphenylhydrazyl was used to study the decomposition of AIBN under the conditions of heterophase polymerisation.[39] In the polymerisation of styrene[40] in the presence of this radical, there was indeed no additional initiation and the decrease of the steady-state rate was much smaller than in the case of the classical DPPH.

Braun and Peschk[41,42] prepared a series of hydrazyl radicals without nitro-groups and investigated their recombination with cyanoisopropyl and polystyryl radicals. The inhibiting activity of the hydrazyl radicals depended not only on their structure but also on the presence of oxygen in the system. The only exception was 2-(2',4',6'-trimethoxycarbonylphenyl)-1,1-diphenylhydrazyl radical, which could be used for quantitative measurements of the rate of initiation, since oxygen did not affect its inhibiting activity and the induction period was directly proportional to the radical concentration. In particular, the rate of initiation of the polymerisation of styrene (with AIBN as the initiator) determined with its aid agrees satisfactorily with the literature data.[3]

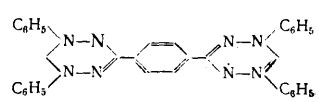
## III. VERDAZYL RADICALS

In the first study[43] devoted to this class of stable radicals, it was already shown that the 1,3,5-triphenylverdazyl radical suppresses the polymerisation of styrene. In subsequent detailed investigations[44,45] of the polymerisation of styrene, methyl methacrylate, and certain other vinyl monomers, the high efficiency of the inhibiting effect of the verdazyl radical and the possibility of using it to determine the rate of chain initiation were established. It was found that the products of the recombination of verdazyl radicals with active radicals are capable of homolytic dissociation with formation of a stable radical (the activation energy for the homolysis is approximately 140 kJ mol$^{-1}$):[46]



where R' is the initiator or polymer radical.

In the polymerisation of certain acrylic monomers (for example, oligourethane acrylate), the regeneration of the verdazyl radical was not observed and the inhibition efficiency appreciably diminished with increase of temperature.[47] In contrast to the 2,4,6-triphenyl-3,4-dehydro-s-tetrazine-1-verdazyl monoradical, the participation of the phenylenebisverdazyl radical



in the reactions entailed a sharp decrease of the rate of polymerisation.

The triphenylverdazyl radical is capable of reacting with acrylonitrile[40] via the double bond with an activation energy of about 45 kJ mol$^{-1}$, which indicates a relatively high

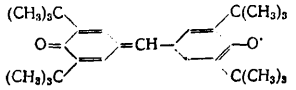
initiating activity of the verdazyl radical compared with many other stable radicals.

As in the case of DPPH, the accuracy of the determination of the rate of decomposition of the initiators with the aid of the triphenyl verdazyl radical depends on the ratio of the inhibitor and initiator concentrations. When a verdazyl radical is employed, this ratio should not exceed 2.[34]

The above characteristic features of the behaviour of verdazyl radicals limit their application to the reliable estimation of various kinetic parameters. The capacity of verdazyl radicals for relatively rapid oxidation by peroxy-compounds [48–50] at comparatively low temperatures (10–20 °C) precludes the determination of the characteristics of the initiation of polymerisation in their presence.

## IV. ARYLOXY-RADICALS

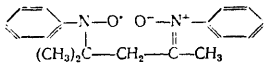
Among the radicals of this class, only the so-called galvinoxy-radical[51]



has been used in polymerisation. The decomposition of azocumene,[52] certain peroxy-compounds,[53–55] and AIBN [56] as well as the mechanism of the thermal polymerisation of deuteriated pentafluorostyrene[57] have been investigated with its aid. The galvinoxy-radical interacts with cyanoisopropyl radicals mainly by recombination. However, owing to the low photochemical and thermal stability of this radical and its ability to react with oxygen,[24] it cannot be used in accurate kinetic measurements.

## V. NITROXY-RADICALS

Until the beginning of the 1960s, only one classical nitroxy-radical, namely Banfield's radical or the nitroxynitroxide radical



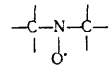
was used as the polymerisation inhibitor and free radical acceptor. Bevington and Ghenem[58] inhibited the polymerisation of styrene and methyl methacrylate with this radical. In air Banfield's radical is relatively unstable, its stability being appreciably higher in an inert atmosphere. The induction period of the polymerisation reaction in the presence of this radical is shorter than the value calculated from the formula $\tau = [X]_0/W_i$, which can be explained by its partial decomposition.

Tudos et al.[59] suggested that $\tau$ diminishes owing to the involvement of the radical in initiation reactions. Only on this hypothesis do the rates of initiation of polymerisation obtained[59,60] agree satisfactorily with literature data.

The influence of Banfield's radical, like, incidentally, that of other inhibitors, on the rate of polymerisation depends on the nature of the monomer and, in copolymerisation, also on the ratio of the concentrations of the monomers employed. Thus in solution in acrylonitrile the radical reacts with the monomer itself and the reaction is autocatalytic.[39] For this reason, Banfield's radical is unsuitable for the determination of the quantitative characteristics of the polymerisation of acrylonitrile. In the copolymerisation of acrylonitrile and styrene with participation of this radical, the stoichiometric inhibition coefficient exceeds unity,[61] which indicates the regeneration of the inhibitor in competition with the additional initiation reaction. At 50 °C and at a relatively low monomer concentration, the contribution of Banfield's radical to chain initiation in the copolymerisation of acrylonitrile with methyl methacrylate in dimethylformamide (DMF) is slight. With increase of temperature and the content of acrylonitrile, the effect becomes appreciable.[62] In the copolymerisation of styrene with maleic anhydride in solutions of acetonitrile, acetone, and tetrahydrofuran (THF) in the presence of Banfield's radical, the induction period in the process increases with decrease in the concentration of the monomers.

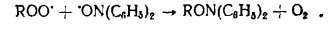
At the end of the induction period the rate of copolymerisation becomes lower than the rate of reaction in the absence of the inhibitor and depends appreciably on the concentration of the latter.[63] These results show that the use of Banfield's radical for accurate measurements of the rate of initiation without taking into account side reactions cannot be regarded as justified.

The successful development of the chemistry of stable radicals during the last twenty years[24,38] has led to the discovery of a new class of extremely stable non-aromatic nitroxy-radicals (iminoxy-radicals) with a localised free-radical centre:[64,65]

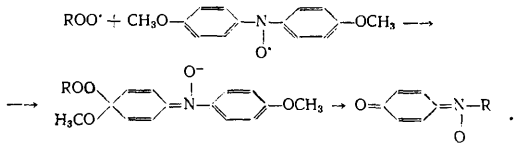


In the first studies[66–72] devoted to the use of nitroxy-radicals of this class as radical counters and antioxidants, interesting features of their behaviour were already observed. It was shown that, in contrast to the classical aromatic nitroxy-radicals, the non-aromatic nitroxy-radicals recombine rapidly with alkyl radicals but do not interact with peroxy-radicals.

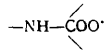
Classical aromatic nitroxy-radicals interact with the radicals ROO'; for example, at 60 °C the rate constant for the reaction of the di-(4-methoxyphenyl)-nitroxy-radical with peroxy-radicals is $6 \times 10^5$ dm$^3$ mol$^{-1}$ s$^{-1}$.[63] It had been suggested earlier[73,74] that aromatic nitroxy-radicals interact with peroxy-radicals in accordance with the mechanism



In our view, the attack by the peroxy-radical in the *para*-position in one of the benzene rings of the diarylnitroxy-radical with formation of a quinonoid structure is more probable:[75,76]



We believe that the proposed mechanism agrees better with experimental data including the accumulation of compounds of the quinonitroxide type in the reaction products.[77] It is noteworthy that non-aromatic nitroxy-radicals can also react with peroxy-radicals if the latter have a favourable chemical structure. Thus the oxidation of primary and secondary aliphatic amines[78] results in the formation of peroxy-radicals of the iminoperoxy-type:



Such radicals interact with non-classical nitroxy-radicals to form the corresponding hydroxylamine with subsequent regeneration of the stable radical:

$$-NH-\underset{\diagdown}{\overset{\diagup}{C}}OO^{\cdot} + \rangle N-O^{\cdot} \rightarrow \rangle NOH + -N=\underset{\diagdown}{\overset{\diagup}{C}} + O_2 ;$$

$$-NH-\underset{\diagdown}{\overset{\diagup}{C}}OO^{\cdot} + \rangle NOH \rightarrow -NH-\underset{\diagdown}{\overset{\diagup}{C}}OOH + \rangle NO^{\cdot}.$$

Analogous results have been obtained in the inhibition of the oxidation of dimethylaminoethyl methacrylate.[79] In the oxidation of the alkyl methacrylates, the active intermediate chain centres are polyperoxy-radicals without reducing properties. Chain termination takes place as a result of the interaction of the nitroxy-radicals with alkyl radicals, the inhibitor not being regenerated. When a tertiary amino-group is introduced into the methacrylate, the chain termination mechanism changes—the above reactions become most important and the nitroxy-radical is regenerated.

The mechanism of the interaction of the nitroxy-radicals with alkyl radicals has been investigated.[80,81] The main product of the reaction of the 2,2,6,6-tetramethyl-4-oxopiperidin-1-yloxy-radical with the cyanoisopropyl radical was an ether derived from a heterocyclic hydroxylamine.

The view that recombination is the only pathway involved in the interaction of nitroxy-radicals with active radicals is widely held. In particular, the unique capacity of nitroxy-radicals for regeneration in reactions where they inhibit the oxidation of olefins, polyolefins, and hydrocarbons has been explained on the basis of this idea.[82-87] It follows from these investigations that the regeneration takes place as a result of the reaction

$$\rangle NOR + ROO^{\cdot} \rightarrow \rangle NO^{\cdot} + \text{products}.$$

However, the results of Shlyapnikov et al.[88] do not agree with these ideas. Experiment has shown that the 2,2,6,6-tetramethyl-4-oxopiperidin-1-yloxy-radical is regenerated approximately $10^3$ times faster than would be the case if this happened solely via the reaction presented above. According to the authors, this is associated with chain termination not only via recombination but also due to disproportionation, which leads to the formation of the hydroxylamine.

The efficiency of nitroxy-radicals as free radical acceptors has stimulated their application in the study of the mechanisms of polymerisation initiation. This application has developed in a number of investigations.[89-96] The authors established that, in the general case, when the nitroxy-radical is added to the monomer–initiator system, the polymerisation is suppressed but the radical is able to react only with some of the initiator radicals, while in the case where peroxides are used it does not interact with the primary radicals at all. For this reason, the products of the reactions of the primary radicals with the monomer are formed in this case in almost quantitative yields. They interact with the nitroxy-radicals and form stable adducts, whose structure has been reliably established. Under certain conditions, the nitroxy-radical can catalyse the decomposition of peroxides.[97]† Thus nitroxy-radicals can be used as effective analytical reagents and information about the fine details of the initiation mechanism can be obtained with their aid.

In the first studies of the influence of classical aromatic nitroxy- and iminoxy-radicals on the rate of radical polymerisation,[98,99] the rate constants for the interaction of the stable radicals with the styrene macroradicals were determined by EPR. The calculations were performed on the assumption that chain termination takes place in 1 : 1 proportions. Furthermore, a study was made of the reactions of stable biradicals with the alkyl radicals formed on decomposition of AIBN in ethylbenzene and dioxan.[100] It was observed that the probability of the recombination of the radical centre depends on the residual unpaired electron in the biradical.[101] The first reaction (with one of the localised free-radical centres) proceeds more readily than the second, which the authors explain within the framework of the adiabatic nature of the recombination reaction.

The interaction of certain mono- and di-radicals with styrene and α-methylstyrene at 100–120 °C has been investigated by EPR.[102] The authors suggest that the stable radicals are consumed in reactions involving addition to the monomer molecules (additional initiation) and in the course of recombination with the active radicals produced. The following mechanism has been proposed for the monoradicals (X):

$$CH_2=\underset{C_6H_5}{\underset{|}{CH}} + X^{\cdot} \xrightarrow{k_M} X-CH_2-\underset{C_6H_5}{\underset{|}{CH}} ;$$

$$R^{\cdot} + X^{\cdot} \xrightarrow{k_X} \text{products}.$$

However, the authors did not take into account the fairly high capacity of styrene for thermal polymerisation, whose rate is high at the temperatures indicated. For this reason, some of the stable radicals should be consumed in reactions with the species initiating the thermal polymerisation. This factor has been taken into account in two investigations[103,104] of the influence of pressure on the reactions occurring in the styrene–iminoxy-radical system at 80 °C. Assuming that the thermal initiation takes place in accordance with Mayo's mechanism,[105] the authors obtained an equation for the rate of consumption of the nitroxy-radical in the monomer:

$$-d[X]/dt = 2k_{DA}[M]^2 + 2k_M[M][X] ,$$

where $k_{DA}$ is the rate constant for the reaction of the iminoxy-radical with the Diels–Alder adduct and [M] is the monomer concentration. The validity of this equation requires additional evidence in view of the uncertainty of the mechanism of the initiation of the thermal polymerisation of styrene[33] and the latest data concerning the influence of iminoxy-radicals on the rate of this reaction.[106,107]

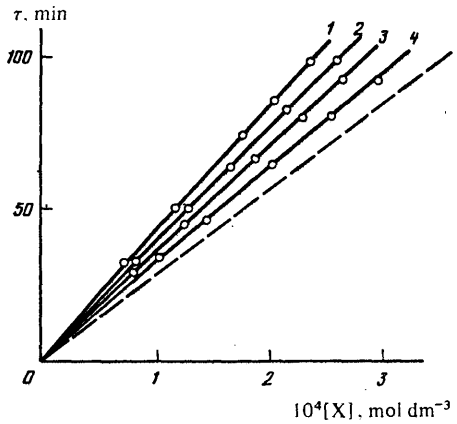
In a study of the propagation of the chloroprene ω-polymer in the presence of iminoxy-radicals,[108] yet another piece of evidence for the free-radical nature of the ω-polymerisation of this monomer was obtained.

The advances in the chemistry of nitroxy-radicals have made it possible to synthesise polymeric free radicals in which the nitroxy-radical forms part of the composition of the polymer chain unit.[109] Such macromolecular stable radicals inhibit effectively the polymerisation of styrene and methyl methacrylate initiated by AIBN [110-112] and also the polymerisation accompanying the synthesis of unsaturated ethers.[113]

The influence of di(4-ethoxyphenyl)nitroxy-radical on the polymerisation of styrene has been investigated.[114] The decrease of the inhibiting activity of the arylnitroxy-radical in the presence of benzoyl peroxide, despite the linear dependence of τ on the concentration of the additive, was observed for the first time in the above study. In contrast to the polymerisation initiated by AIBN, a slower increase in the rate of reaction during the induction period and a decrease of the steady-state rate with increase of the arylnitroxy-radical concentration were then observed. It will be shown below that these effects are associated with the interaction of the benzoate radical with the aryl nitroxy-radical.

† This observation was subsequently used by one of the present authors for the selective inhibition of certain undesirable oxidation reactions—see, for example, Maslov et al.[154]

The 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-yloxy-radical[115] was one of the first nitroxy-radicals used as the counter of active centres in the polymerisation of tetrafluoroethylene.[116] The possibility of determining the rate of chain initiation with the aid of this iminoxy-radical was justified in the above investigation by the fact that the induction period is directly proportional to the inhibitor concentration and the polymerisation is not retarded at the end of the inhibition period. A 1 : 1 stoichiometry of chain termination was adopted, as in many other studies.[117–125]




Dependence of the induction period in the polymerisation of styrene on the concentration of the iminoxy-radical: 1) 2,2,6,6-tetramethyl-4-oxopiperidine-1-yloxy-ester of α-cyano-ββ′-diphenylacrylic acid; 2) 2,2,6,6-tetramethyl-4-salicylideneaminopiperidin-1-yloxy-radical; 3) 2,2,6,6-tetramethyl-4-stearyliminopiperidin-1-yloxy-radical; 4) 2,2,6,6-tetramethyl-4-benzoylpiperidin-1-yloxy-radical; initiator—azobisisobutyronitrile ($3 \times 10^{-2}$ mol dm$^{-3}$); 45 °C; the dashed line corresponds to $\mu = 1$.

The reaction of the 2,2,6,6-tetramethyl-4-oxopiperidin-1-yloxy-radical[126] with primary and polymeric radicals in the inhibition of the polymerisation of styrene and methyl methacrylate has been studied.[127] The inhibition mechanism proposed by the authors includes a stage involving the recombination of the active and stable radicals with formation of the corresponding ethers. This conclusion is confirmed by the fact that the ether does not influence the rate of polymerisation, while the reduced radical (hydroxylamine) induces a marked decrease in the rate of the process. In fact, there is no retardation of the polymerisation at the end of the induction period.

At the same time there exist data in conflict with the idea of a simple stoichiometry of chain termination. Comparative estimation of the inhibiting activities of the iminoxy- and arylnitroxy-radicals in the initiated polymerisation of styrene showed[128] that the stoichiometries of the reactions with polystyrene radicals are the same for different classes of nitroxy-radicals. However, this fact was not explained.

The study of the inhibiting properties of the 2,2,6,6-tetramethyl-4-oxopiperidin-1-yloxy- and 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-yloxy-radicals in the polymerisation of oligourethaneacrylate[47] showed that the former radical induces under identical conditions a longer induction period than the latter. This means that the 2,4-bis(2,2,6,6-tetramethyl-4-ureidopiperidin-1-yloxy)tolylene biradical inhibits the polymerisation of oligourethaneacrylate more effectively than would be the case for simple stoichiometry of the termination reaction.

In the inhibition of the copolymerisation of styrene with acrylonitrile by the 2,2,6,6-tetramethylpiperidine-1-yloxy-radical, it was found[61] that the stoichiometric inhibition coefficient depends on the nature of the initiator and is much greater than unity when AIBN is used. According to Shlyapnikov et al.,[129] the occurrence of side reactions hinders the application of the inhibitor method to the determination of the relatively low rates of the chain initiation reactions in processes involving the degradation of polymers in an inert atmosphere.

In order to refine the mechanism and find the quantitative characteristics of the inhibition by iminoxy-radicals, it is most convenient to study their influence on the polymerisation of thoroughly investigated monomers (styrene and acrylate and methacrylate esters) in the presence of initiators with known rates of decomposition (AIBN and benzoyl peroxide). In the polymerisation initiated by AIBN, the rate of consumption of stable radicals during the inhibition period is lower in all the monomers than the rate of initiation, i.e. $\mu > 1$ [130–133] (see Figure). Such increase of $\mu$ can be explained, for example, by the regeneration of the inhibitor. However, in certain cases when the period $\tau$ has come to an end, the rate of polymerisation becomes lower than the rate of the non-inhibited process. With increase of the concentration of the additive, the induction period shortens, which is apparently caused by the addition of the stable radical to the monomer at the double bond (i.e. by the additional initiation).

Thus the effective inhibition of polymerisation by iminoxy-radicals is accompanied by complex reactions. In order to elucidate certain details of the inhibition process, the influence of ethers $R_0$–X ($R_0$ is a primary radical) and hydroxylamines X–H on the polymerisation has been investigated[155] and it has been established that ethers do not affect the polymerisation kinetics, while the rate of the process diminishes somewhat in the presence of hydroxylamines. Consequently the regeneration can be explained by the fact that some of the iminoxy-radicals disproportionate in a reaction with active radicals, forming nitroso-compounds.[134] The latter suppress the polymerisation, each terminating two kinetic chains per inhibitor molecule. Apparently the involvement of iminoxy-radicals in this stage is in fact responsible for the increase of the stoichiometric coefficient, while the decrease of the steady-state rate of polymerisation is associated with chain termination by hydroxylamines.

The radical-chain mechanism of the polymerisation of vinyl monomers, initiated by AIBN, in the presence of added iminoxy-radicals can be represented in the following way on the basis of the foregoing:

$$\text{AIBN} \rightarrow 2R_0^{\cdot} + N_2\uparrow ; \qquad \text{(I)}$$

$$R_0^{\cdot} + M \xrightarrow{k_i} R^{\cdot} ; \qquad \text{(II)}$$

$$R^{\cdot} + M \xrightarrow{k_p} R^{\cdot} ; \qquad \text{(III)}$$

$$X + M \xrightarrow{k_i} R^{\cdot} ; \qquad \text{(IV)}$$

$$R^{\cdot} + X \xrightarrow{k_t} RX ; \qquad \text{(V)}$$

$$X + R^{\cdot} \xrightarrow{k_t} XH + \text{inactive products;} \qquad \text{(VI)}$$

$$X + M \xrightarrow{k_s} R^1\text{—N=O} + HM ; \qquad \text{(VII)}$$

$$R^1\text{—N=O} + R^{\cdot} \rightarrow R^1\text{—N(O}^{\cdot}\text{)—R} ; \qquad \text{(VIII)}$$

$$R^1\text{—}\underset{\underset{O^\cdot}{|}}{N}\text{—}R + R^\cdot \rightarrow R^1 - \underset{\underset{OR}{|}}{N}\text{—}R\ ; \qquad (IX)$$

$$XH + R^\cdot \rightarrow X^\cdot + RH\ ; \qquad (X)$$

$$R^\cdot + R^\cdot \rightarrow \text{polymer}. \qquad (XI)$$

The additional initiation with the aid of the stable radical proceeds slowly ($k_i \cong 10^{-6}$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 60 °C), the secondary inhibition is slight, and in the course of the induction period the contribution by the quadratic termination to the overall chain termination is small. For these reasons, disregarding reactions (IV), (X), and (XI), the kinetic equation describing the consumption of the iminoxy-radicals assumes the following form:

$$-d[X]/dt = W_i(k_1 + k_2 + k_3)/(k_1 + k_2 + 2k_3). \qquad (1)$$

The inhibitor should be consumed in accordance with a linear law at a rate lower than that of initiation, which has been confirmed satisfactorily by experimental data. The stoichiometric inhibition coefficients are calculated in these cases from the formula

$$\mu = 1 + \frac{2k_3}{k_1 + k_2 + k_3}\ . \qquad (2)$$

The time variation of the rate of inhibited polymerisation obeys the Bagdasar'yan–Bamford equation:

$$-\frac{1}{\varphi} + \ln\frac{1+\varphi}{1-\varphi} = (k_X + k_3)[R]_\infty t + \text{const}\ , \qquad (3)$$

where $\phi = W_t/W_\infty$ is the ratio of the rates of polymerisation at any instant $W_t$ and the steady-state $W_\infty$, $[R]_\infty$ is the steady-state concentration of the polymeric radicals, and $k_X = k_4 + k_5$. Eqns.(1) and (2) are valid at relatively low temperatures (40–60 °C). The consumption of iminoxy-radicals increases with increasing temperature owing to the suppression of the thermal initiation and their addition to the monomer, the experimental quantity $\mu_{exp}$ therefore diminishes. The contribution of these reactions can be taken into account by calculating the rate of consumption of the inhibitor in the monomer at an elevated temperature $\omega_0 = \{-d[X]/dt\}_0$. Then, denoting the rate of consumption of iminoxy-radicals in the inhibition reaction by $\omega = d[X]/dt$, we obtain

$$W_i = \mu_{exp}(\omega_0 + \omega), \qquad (4)$$

where $\mu_{exp}$ is the experimental (apparent) stoichiometric inhibition coefficient. An expression for the true value of $\mu$ can be readily obtained from Eqn.(3):

$$\mu = \frac{W_i\mu_{exp}}{W_i - \omega_0\mu_{exp}} \qquad (5)$$

The set of equations (2), (3), and (5) makes it possible to estimate the inhibition rate constant $k_X$ and the rate constant for the regeneration of the inhibitor $k_3$ as well as the activation energies $E$ for these reactions (see Table). It is essential to note that the relative errors of the tabulated rate constants and activation energies are approximately 10 and 15% respectively. The differences are most probably associated with the different structures of the stable radicals investigated. However, hitherto it has not been possible to establish a reliable correlation between the chemical structure of the iminoxy-radicals and the parameters noted above, characterising their inhibiting effect. Comparison of the quantities $k_X$, $k_3$, $E_X$, and $E_3$ suggests that the substituent exerts the main influence on the pre-exponential factor (i.e. on the steric factor) and not on the activation energy.

The tabulated $k_X$ differ from the literature data. The constants for the interaction of nitroxy-radicals with primary and polymeric radicals found by different workers vary from $10^4$ to $10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$.[98,114,128,135] This scatter is not surprising, since in many cases no account was taken of the details of the inhibition mechanism associated with the complex stoichiometry of the chain termination, the inhibitor generation, the additional initiation, the influence of the type of initiation and of the nature of the initiator, the characteristic features of oxidative polymerisation, etc.

Kinetic parameters of the inhibition of the polymerisation of styrene and methyl methacrylate by iminoxy-radicals (60 °C, initiator—AIBN).* [130–133,155]

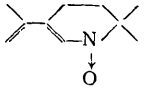
| Radical | $10^{-5}k_X$, dm$^3$mol$^{-1}$s$^{-1}$ | $10^{-5}k_3$, dm$^3$ mol$^{-1}$ s$^{-1}$ | $E_X$, kJ mol$^{-1}$ | $E_3$, kJ mol$^{-1}$ |
|---|---|---|---|---|
| (A) | 5.0; 6.4 | 1.9; 1.6 | 16; 12 | 26; 23 |
| (B) | 7.0; 6.8 | 1.5; 1.2 | 13; 14 | 26; 29 |
| (C) | 2.0; 4.9 | 0.7; 1.6 | 12; 10 | 21; 25 |
| (D) | 2.5; 6.8 | 0.8; 1.2 | 13; 13 | 23; 27 |
| (E) | 3.5; — | 0.7; — | 11; — | 25; — |
| (F) | 3.0; 6.0 | 0.2; — | 16; 17 | 36; — |

Notation: (A) = 2,2,6,6-tetramethyl-4-oxopiperidin-1-yloxy-ester of α-cyano-ββ′-diphenylacrylic acid; (B) = 2,2,6,6-tetramethyl-4-salicylideneaminopiperidin-1-yloxy-radical; (C) 2,2,6,6-tetramethyl-4-palmitylimino-piperidin-1-yloxy-radical; (D) = 2,2,6,6-tetramethyl-4-stearyliminopiperidin-1-yloxy-radical; (E) = 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-yloxy-radical; (F) = 2,2,6,6-tetramethyl-4-benzoylpiperidin-1-yloxy-radical.

*The first and second numbers represent respectively the data for styrene and methyl methacrylate.

The kinetics and mechanism of the polymerisation inhibited by nitroxy-radicals change significantly on passing from initiation by azo-compounds to initiation by peroxy-radicals. The mechanism of the interaction of iminoxy-radicals with peroxy-radicals is determined by the chemical structure of the latter and the nature of the solvent. Thus the rates of decomposition of benzoyl peroxide (BP) in DMF and of t-butyl and dicumenyl peroxides in benzene are independent of the presence of iminoxy-radicals in the mixture.[136,137] On the other hand, the decomposition of acetylphenyl peroxide in carbon tetrachloride[138] and of dicyclohexyl peroxydicarbonate in benzene and chlorobenzene[139] is accelerated with formation of free-radicals and non-radical products.

At concentrations of the iminoxy-radicals exceeding the BP concentration by approximately a factor of two, the induced decomposition of the peroxide in the monomer takes place with formation of a heterocyclic nitroxide (nitrone)



and benzoic acid.[140]

Under polymerisation conditions where [BP] ≫ [X], the formation of side products is apparently suppressed and the induced decomposition accompanied by the formation of a donor–acceptor complex $Q_1$ becomes the main process:[141]

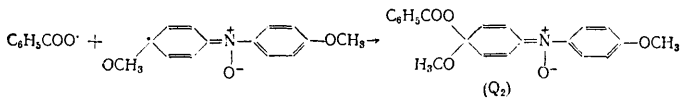
$$BP + X \rightleftarrows Q_1 \rightleftarrows 2C_6H_5COO^\cdot + X\ .$$

The effective rate constants for the decomposition of the BP bound in the complex are approximately $10^2$ dm$^3$ mol$^{-1}$ s$^{-1}$ in styrene and $5 \times 10^3$ dm$^3$ mol$^{-1}$ s$^{-1}$ in methyl methacrylate (60 °C). The effective activation energy for the decomposition reaction is about 80 kJ mol$^{-1}$, which is appreciably lower

than for the free initiator molecule (125 kJ $mol^{-1}$). Thus iminoxy-radicals are unsuitable for the determination of the rate of chain initiation by peroxide initiators.

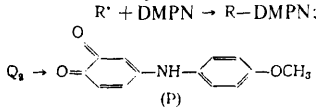
The significant differences between the reactivities of iminoxy-radicals and aromatic nitroxy-radicals[24,142] lead to their different effects on the kinetics of polymerisation initiated by peroxides. Whereas the role of iminoxy-radicals reduces to the acceleration of the decomposition of BP (naturally apart from the inhibition itself), nitroxy-radicals [for example, di(4-methoxyphenyl)nitroxy-radicals (DMPN)] interact with BP to form non-radical products.[143] The reaction in the monomers proceeds via a more complex multistage mechanism:

$$BP + DMPN \rightarrow 2C_6H_5COO^{\cdot} + DMPN:$$

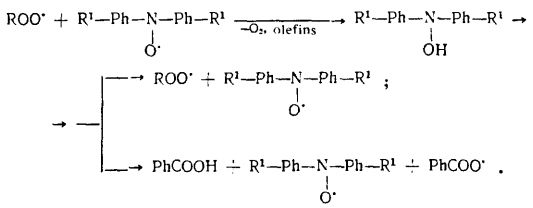


$$C_6H_5COO^{\cdot} + M \rightarrow R^{\cdot}$$

$$R^{\cdot} + DMPN \rightarrow R{-}DMPN:$$



The aminoquinone (P) formed is a probable polymerisation inhibitor. It follows from the above mechanism that, whereas in an inert atmosphere two stable radicals are consumed per BP molecule, in the presence of air the stoichiometry changes owing to the regeneration of the arylnitroxy-radical:[73,128,144]



The change in stoichiometry does not lead to new kinetic effects. At the end of the induction period induced by the presence of the aminoquinone, the polymerisation proceeds at a constant rate $W_\infty$, which is lower than the rate of the non-inhibited reaction $W$.

The following equation corresponds to the radical-chain polymerisation mechanism in the presence of the aminoquinone and with allowance for secondary inhibition:[130]

$$-\frac{1}{\varphi_t} - \ln(1-\varphi_t) + (1-\varphi_\infty^2)\ln\varphi_t + \varphi_\infty^2 \ln\left(\varphi_t - \frac{1}{\varphi_\infty^2}\right) = \frac{k_X}{k_p}\frac{W_\infty}{M}t + A,$$

where $\phi_t = W_t/W_\infty$, $\phi_\infty = W_\infty/W$, and $A$ is a constant. The inhibition constants $k_X$ for different monomers are in the range $10^4$–$10^5$ $dm^3$ $mol^{-1}$ $s^{-1}$ (60 °C) and the activation energy for the inhibition reaction is 23 kJ $mol^{-1}$.

## VI. RADICAL-ANIONS

In contrast to neutral stable radicals, charged radicals usually initiate ionic polymerisation.[145,146] The initiating activity of radical-anions depends on the difference between the electron affinities of the monomer and the initiator. The radical-anions formed from compounds with a very high electron affinity can therefore prove to be incapable of initiating anionic polymerisation. Having an excess charge, the radical-anions usually possess electron-donating properties and are involved in various charge-transfer reactions.

The influence of radical-anions on the polymerisation of vinyl monomers via a radical mechanism has been investigated in relation to the effect of tetracyanoquinodimethane salts, which dissociate in solution with formation of the tetracyanoquinodimethane radical-anion $TCQM^{\cdot-}$. When the polymerisation is initiated by benzoyl peroxide, the introduction into the solution of the lithium salt of tetracyanoquinodimethane (Li TCQM) leads to a sharp acceleration of the polymerisation and a decrease in the molecular weight of the polymer. An increase in the rate was observed only in those cases where the concentration of the salt did not exceed that of the peroxide by a factor greater than two and the highest rate of the process was attained for equal contents of Li TCQM and BP.[147–150]

Studies of the kinetics of the polymerisation and the interaction of BP and $TCQM^{\cdot-}$ showed that a one-electron transfer reaction takes place between the radical-anion and the peroxide molecule with subsequent reactions between the resulting neutral TCQM and the benzoate anion $R^-$ and also between the benzoate radical $R^{\cdot}$ and yet another $TCQM^{\cdot-}$ radical-anion:

$$TCQM^{\cdot-} + BP \rightarrow R^{\cdot} + R^- + TCQM:$$

$$TCQM^{\cdot-} + R^{\cdot} \rightarrow Q^-;$$

$$TCQM + R^- \rightarrow Q^-.$$

These reactions take place at a high rate even before the onset of polymerisation. The initiating radicals are formed in the oxidation-reduction interaction of the intermediates with the BP molecules which fail to react ($\overline{BP}$):

$$\overline{BP} + Q^- \xrightarrow{k_R} R^{\cdot} + R^- + R_Q^{\cdot}$$

The polymerisation is initiated by the BP–Li TCQM system by a factor of several tens faster than as a result of the thermal decomposition of BP.

If the initial Li TCQM concentration is greater than twice the peroxide concentration, then free $TCQM^{\cdot-}$ radical-anions remain in the reaction system and inhibit the polymerisation.

The study of the reactions of various organic peroxides with the $TCQM^{\cdot-}$ radical-anion has shown that, in conformity with the mechanism proposed, the radical-anion interacts only with those peroxides which possess a sufficiently high electron-accepting capacity (benzoyl and lauryl peroxide). Otherwise $TCQM^{\cdot-}$ only exhibits the polymerisation (cumenyl peroxide). In the presence of lauryl peroxide, whose electron-accepting capacity is lower than that of BP, the rate of initiation of the polymerisation diminishes.

The initiation of polymerisation by the peroxide–$TCQM^{\cdot-}$ radical-anion system is characterised by a low activation energy (~40 kJ $mol^{-1}$), which makes it possible to carry out the reaction at a high rate and a relatively low temperature.

The possibility that radical-anions can assume the role of radical polymerisation inhibitors was first demonstrated in relation to the radical-anion salt of 7,7,8,8-tetracyanoquinodimethane with dimethylviologen.[151] It was found that $TCQM^{\cdot-}$ inhibits effectively the polymerisation of styrene, acrylate and methacrylate esters, and acrylonitrile, giving rise to distinct induction periods.[152] It was established that $TCQM^{\cdot-}$ interacts not only with active radicals, inhibiting polymerisation, but also with monomer molecules, which leads to the generation of new active centres, which are immediately terminated by the radical-anion. Such additional initiation induces a relative shortening of the induction period with increase in the inhibitor concentration. The rate constant for the additional initiation $k_i$ depends significantly on the nature of the monomer and diminishes in the sequence styrene > methyl methacrylate > methyl acrylate.

The radical-anion complexes dissociate in solution in different ways depending on the nature of the cation, the concentration, the composition of the medium, and temperature. In the general case the $TCQM^{\cdot-}$ radical-anion exists in solution in the form of both free radical-anions and ion pairs, which have different reactivities. It has been shown that the additional inhibition is induced only by the $TCQM^{\cdot-}$ radical-anions present in solution in the form of ion pairs with a cation, while free-radical-anions are more active in the inhibition reaction.[153] A change in the composition of the reaction medium influences the degree of dissociation of the $TCQM^{\cdot-}$ complexes and hence the contribution of the additional initiation to the overall reaction kinetics. As a result, the duration of the inhibition of the polymerisation by the $TCQM^{\cdot-}$ radical-anions is determined not only by the ratio of the inhibitor concentration and the rate of initiation but also by factors influencing the degree of dissociation of the radical-anion salts.

The dependence of the duration of the induction period in the polymerisation of styrene on the TCQM concentration is fairly complex and is determined by the equation[152]

$$\tau = [2k_{decomp}f\alpha(1-\gamma)]^{-1}\ln\left\{1-\alpha(1-\gamma)\frac{[X]_0}{[I_0]}\right\},$$

where $\alpha = k_i[M]/k_{decomp}f$, $k_i$ is the rate constant for the additional initiation of the polymerisation by the ion pairs involving the $TCQM^{\cdot-}$ radical-anion, $k_{decomp}$ the rate constant for the initiator decomposition reaction, $f$ the efficiency of the initiation, and $[I]_0$ and $[X]_0$ are the initial concentrations of the initiator (AIBN in the study indicated) and the TCQM radical-anion salts.

As a result of the additional initiation reaction, the time variation of the rate of the inhibited polymerisation no longer obeys the Bagdasar'yan–Bamford equation[3] and is described by the more complex expression[151]

$$-2\ln(\varphi_t-\theta)-\left(\frac{1}{\theta}-1\right)\ln(1-\varphi_t)+\left(\frac{1}{\theta}+1\right)\ln(1-\varphi_t)+$$
$$+0.5\left(\frac{1}{\theta^2}-1\right)\ln\left|\frac{\varphi_t-\theta}{\varphi_t+\theta}\right|=\frac{k_X}{k_p}\frac{W_\infty}{M}\left(\frac{1}{\theta}-\theta\right)t+\text{const},$$

where $\theta = k_i[M]/k_X[R]_\infty$, $\phi_t = W_t/W_\infty$, $W_t$ is the rate of polymerisation at time $t$, and $W_\infty$ and $[R]_\infty$ are the steady-state rate and concentration of polymeric radicals.

The plot of the reduced rate of polymerisation $\phi_t$ against time is represented by S-shaped curves with a point of inflection. The parameter $\theta$ is determined from the reduced rate of polymerisation at this point ($\phi_{pi}$) from the equation

$$\theta^3-\frac{2\varphi_{pi}}{1+\varphi_{pi}^2}\theta^2-\frac{3\varphi_{pi}^4-\varphi_{pi}^2}{1+\varphi_{pi}^2}\theta-\frac{\varphi_{pi}^5-2\varphi_{pi}^3-\varphi_{pi}}{1+\varphi_{pi}^2}=0.$$

The inhibition constants $k_X/k_P$ are $10^3$–$10^4$ and vary within wide limits depending on the nature of the cation, the solvent, and the monomer, as well as temperature. Furthermore, they decrease with increase of the inhibitor concentration, while the additional initiation constants $k_i$ increase.

The interaction of the $TCQM^{\cdot-}$ radical-anions with macroradicals proceeds via different mechanisms. Together with addition, there is a possibility of electron transfer from the radical-anion to a macroradical having more pronounced electron-accepting properties. Inhibition via the electron transfer mechanism is most likely in the polymerisation of monomers whose polymeric radicals have a higher electron affinity, i.e. the rate of reaction increases in the monomer sequence styrene < methyl methacrylate < methyl acrylate. As a result of electron transfer, the radical-anion is converted into neutral TCQM, which is itself capable of terminating the reaction chains or, by reacting with the electron-donating solvent (for example, DMF), it is reconverted into the radical-anion.[152]

Thus the reactions involving the regeneration of the inhibitor are characteristic of the inhibition of the polymerisation of the methacrylic and especially acrylic monomers by the $TCQM^{\cdot-}$ radical-anion, which is manifested by an increase in the induction period and a change in the sign of the curvature of the plot of $\tau$ aginst [X].

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# Vinylphenols and Oligomers and Polymers Based on Them

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The review deals with the methods of synthesis of alkenylphenols and their derivatives whose ethylene bond is conjugated with the benzene ring; data are presented on the polymerisation, copolymerisation, and polycondensation of these compounds and also on the applications of polymeric materials based on them.
The bibliography includes 189 references.

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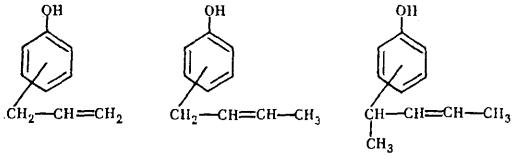
## I. INTRODUCTION

The interest in the chemistry of alkenylphenols is due to the fact that their structure contains functional groups of different nature and that reactive oligomers, polymers, and copolymers exhibiting a tendency towards further chemical reactions, particularly in the material moulding stage, can be obtained by standard oligomerisation, polymerisation, copolymerisation, and polycondensation methods; the evolution of volatile products is not observed in their processing. This approach to the preparation of polymers is extremely valuable in the manufacture of materials capable of being used under extreme operating conditions (thermostable and heat resistant plastics, polymers with three-dimensional structures, etc.).

Alkenylphenols are also of independent interest for the chemical modification of industrial polymers during their synthesis and processing.

Vinylphenol oligomers, polymers, and copolymers are used to prepare epoxyresins, in thermoplastic and thermoreactive compositions, in glues, in the manufacture of laminated plastics, press powders and varnishes, cast articles, and adhesives, in the manufacture of laminated electrically insulating materials, as anti-oxidants for rubbers, resins, and oils, etc.

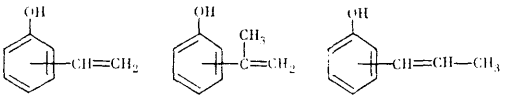
From the standpoint of their reactivity in oligomerisation, polymerisation, and copolymerisation reactions, alkenylphenols can be divided into two main groups. The first group includes alkenylphenols where the ethylene bond of the alkenyl group is not conjugated with the benzene ring, for example:



Alkenylphenols of this series are synthesised by the interaction of phenol or alkylphenol with allyl or methylallyl halides or the corresponding alcohols and with conjugated and non-conjugated dienes in the presence of various catalysts.[1]

Although alkenylphenols of this type can be synthesised comparatively readily, they have not found extensive applications in the syntheses of oligomers and polymers in view of the low reactivity of the allyl group in polyaddition reactions. Alkenylphenols of this type will not therefore be considered in the present review.

The second group include alkenylphenols in which the ethylene bond of the alkenyl group is conjugated with the benzene ring. Typical representatives of this series are vinyl-, isopropenyl-, and propenyl-phenols:



The double bond in alkenylphenols of this series is highly reactive (especially in vinylphenol), which complicates their synthesis and isolation in a pure form.

Vinyl- and isopropenyl-phenols are used to synthesise various reactive oligomers and to modify polymers manufactured industrially. There has been a considerable growth of interest in vinylphenols during the last few years, which is indicated by the numerous publications, mainly patents (especially in Japan, the Federal Republic of Germany, USA, USSR, England, etc.).

The available literature data on the methods of synthesis, properties, and practical applications of vinylphenols and the oligomers and polymers based on them are surveyed and described for the first time in the present review.

## II. SYNTHESIS OF VINYLPHENOLS

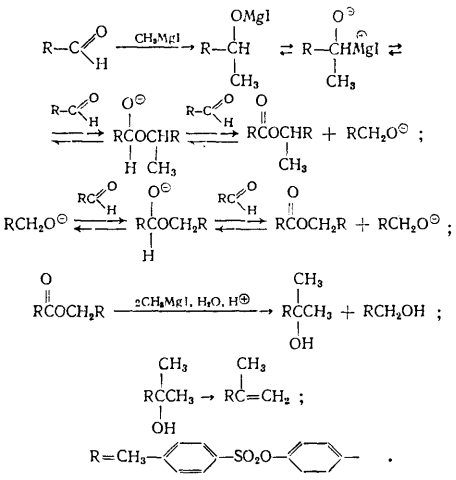
As early as 1931, it was shown that *o*-vinylphenol can be obtained by condensing phenol with epoxyethane, ethylenechlorohydrin,[2] or vinyl acetate[3] with subsequent dehydration of the resulting 2-phenoxyethyl alcohol or the rearrangement of phenyl vinyl ether. However, in practice it is difficult to obtain vinylphenol under these conditions.[4-6] An alcohol which is readily dehydrated to *p*-vinylphenol has been synthesised by the reaction of *p*-hydroxybenzaldehyde with $CH_3MgI$.[7]

*m*-Vinylphenol can be obtained in 50% yield by dehydrating *m*-hydroxyphenylmethylmethanol at 300 °C on activated alumina, but the initial alcohol is difficult to obtain.[8]

A method of synthesis of *p*-vinylphenol by cracking 1,1-bis(4-hydroxyphenyl)ethane in the presence of aluminosilicate catalysts at 550–560 °C (yield 60%) was proposed in 1960.[9,10] *o*-Vinylphenol is obtained analogously by the pyrolysis of 2,4-dimethylbenzo-1,3-dioxan at 400–450 °C.[11] The pyrolytic methods of synthesising vinylphenol have attracted attention because of their simplicity and the wide variety of initial compounds which can be used. Thus

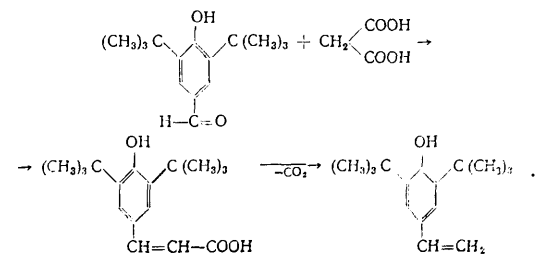
o-vinylphenol can be obtained by the pyrolysis of cyclo-octa-1,3,5-triene-7-one and the product of its irradiation—*cis*-bicyclo[4.2.0]octa-4,7-dien-2-one.[12] Benzene and acetone are formed together with the required product during the pyrolysis. The cracking of 1,1-bis(4-hydroxy-5-methylphenol)ethane leads to 2-methyl-4-vinylphenol.[9] Both *p*-vinylphenol and 2-methyl-4-vinylphenol synthesised in this way readily polymerised on standing in air. The above reaction was later carried out in the presence of iron, manganese, cobalt, copper, thorium, antimony, vanadium, tin, molybdenum, and tungsten oxides. $Na_2CO_3$, MgO, CaO, BaO, and $Cr_2O_3$ have been used as promoting agents. In the presence of iron–chromium catalysts promoted by $K_2CO_3$, a high degree of conversion of the starting material is attained (92–94%) and is accompanied by a high selectivity in the formation of *p*-vinylphenol (85–89%).[13]

It is of interest to note that the organomagnesium synthesis of vinylphenol does not always lead to the desired results. For example, when an attempt was made to synthesise *p*-vinylphenol by the reaction of 4-(4-$CH_3C_6H_4SO_2O$)$C_6H_4CHO$ with $CH_3MgI$, *p*-isopropenylphenol was obtained instead of the expected product,[14] probably in accordance with the following scheme:

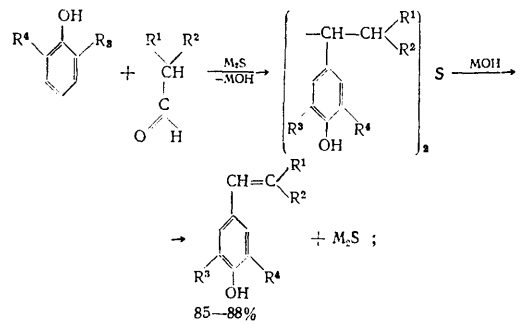


The isolation of vinylphenols in a pure form from the products of the dehydrogenation of ethylphenols and of the cracking of 1,1-bis(4-hydroxyphenyl)ethane presents considerable difficulties. In order to prevent tar formation, it is recommended that the vinylphenols be diluted with an equal volume of ethylene glycol[15] and admixtures of phenol, ethylphenols, hydrocarbons, and vinylphenol polymers are removed from vinylphenols by means of contact counter-current apparatus with aqueous alkaline solutions and organic solvents immiscible with water.[16]

Some methods of synthesis of vinylphenols (decarboxylation of the corresponding hydroxycinnamic acid, dehydration of hydroxyphenylmethylmethanols, pyrolysis of 2,4-dimethylbenzo-1,3-dioxan, etc.) have been described in a monograph.[17] However, since it is difficult to obtain the starting materials, these methods are used only for laboratory purposes. For example, the synthesis of 2,6-di-t-butyl-4-vinylphenol by the condensation of 2,6-di-t-butyl-4-hydroxybenzaldehyde with malonic acid and subsequent decarboxylation of the resulting substituted cinnamic acid has been described:[18]



2,6-Di-t-butyl-4-vinylphenol and its β-alkyl-substituted derivatives can also be obtained[19] by the condensation of 2,6-di-t-butylphenol with aldehydes in the presence of an alkali metal sulphide and the subsequent decomposition of the reaction products in accordance with the scheme



M = alkali metal; $R^1$, $R^2$ = H, Alk; $R^3$, $R^4$ = t-$C_4H_9$, etc.

The methods of synthesis of isopropenylphenols are of independent interest. Much attention has been devoted in the literature to their development. According to literature data, the catalytic decomposition of di(hydroxyphenyl)-propane, the alkylation of phenols by acetylene homologues, the dehydrogenation of alkylphenols, etc. are of greatest interest.

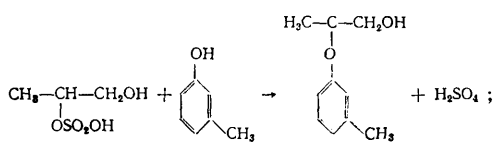
The rearrangement of isopropenyl ethers of aromatic hydroxy-compounds leads to *o*-isopropenylphenols. The reaction takes place in the presence of 10% sulphuric acid in glacial acetic acid.[20] The initial ethers can be obtained either by treating isopropenyl bromide with the corresponding potassium phenoxide or from phenol and allyl alcohol. In the latter case the isopropenyl ethers need not be isolated and a mixture of allyl alcohol and the aromatic hydroxy-compound can be used immediately for the synthesis of *o*-isopropenylphenols.

The mechanism of the synthesis of isopropenylphenols, in particular 6-isopropenyl-3-methylphenol from *m*-cresol and allyl alcohol under the influence of concentrated sulphuric acid, is represented in the following manner:[3,20]

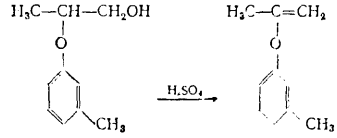
a) the addition of sulphuric acid to allyl alcohol with formation of 1-hydroxymethylethylsulphuric acid:

$$H_2C{=}CH{-}CH_2OH + H_2SO_4 \rightarrow CH_3CH(CH_2OH)OSO_2OH\ ;$$

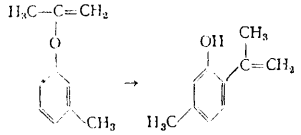
b) the interaction of 1-hydroxymethylethylsulphuric acid with *m*-cresol:



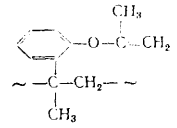
c) the dehydration of the resulting ether by concentrated sulphuric acid:



d) the rearrangement of the unsaturated ether to 6-isopropenyl-3-methylphenol:

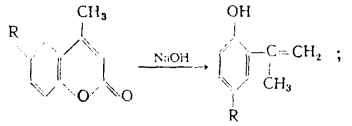


When phenol was allowed to react with methylacetylene in the presence of potassium hydroxide,[21] isopropenyl phenyl ether was isolated as the main product in 57% yield. Isopropenyl ether of o-isopropenylphenol and its trimerisation products (with a molecular weight of ~500), corresponding to the general formula



were also obtained.

Finally o-isopropenylphenol and its ring-substituted derivatives can be obtained by the reaction of 4-methylcoumarin and its derivatives, which are intramolecular phenol esters:[22]



R=H, $CH_3$, $C_2H_5$, iso-$C_3H_7$, $OCH_3$, Cl, Br

p-Isopropenylphenols are not usually obtained from the alkenyl ethers of aromatic hydroxy-compounds; other reactions are used for this synthesis, in the first place the decomposition of di(hydroxyphenyl)propane. Isopropenylphenols are normally always formed in small amounts (up to 3%) as side products in the manufacture of di(hydroxyphenyl)propane (bisphenol-A), which is based on the condensation of phenol with acetone in the presence of acid or alkaline catalysts.[23] It has been suggested in the literature[24,25] that p-isopropenylphenol is an intermediate in the condensation of phenol with acetone under the conditions indicated. Indeed the possibility of obtaining di(hydroxyphenyl)propane from p-isopropenylphenol in the presence of acid or alkaline catalysts has been demonstrated.[26-28]

A study of the thermal decomposition of di(hydroxyphenyl)methane derivatives showed[24] that one mole of the initial reactant gives rise to one mole of phenol, ~0.5 of a mole of an alkylphenol, and tarry substances. A distillate consisting of phenol, p-isopropylphenol, and tarry products has been obtained from di(hydroxyphenyl)propane in ~80% yield by distillation at atmospheric pressure. The authors[24] believe that the decomposition of di(hydroxyphenyl)propane proceeds initially with the formation of phenol and p-isopropenylphenol and its subsequent disproportionation to p-isopropylphenol and hydrogen-depleted tarry substances. This mechanism of the disproportionation has not been proved.[25]

The decomposition of di(hydroxyphenyl)propane at 100 °C in the presence of concentrated hydrochloric acid leads to a mixture of complex composition consisting of phenol, saturated p-isopropenylphenol dimers, and tarry products. Monomeric p-isopropenylphenol was not detected under these conditions.[24]

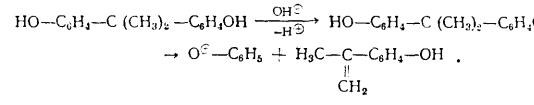
The decomposition of di(hydroxyphenyl)propane in a flow reactor in the presence of an aluminosilicate catalyst at 550 °C and after a contact time of 0.03 s (diluent—water vapour) leads to the formation of p-isopropenylphenol and phenol.[9] However, owing to the disproportionation and isomerisation side reactions, the yield of the required products does not exceed ~46%.

Thus the use of acid catalysts in the cracking of di(hydroxyphenyl)propane promotes the conversion of the cracking products into tars, reducing thereby the yield of p-isopropenylphenol. Side reactions such as disproportionation or oligomerisation of isopropenylphenols takes place to a much lesser extent in the cracking of di(hydroxyphenyl)propane in the presence of alkalis. The use of a vacuum and the continuous removal of the cracking product from the reaction zone also promote an increase in the yield of p-isopropenylphenol under these conditions.

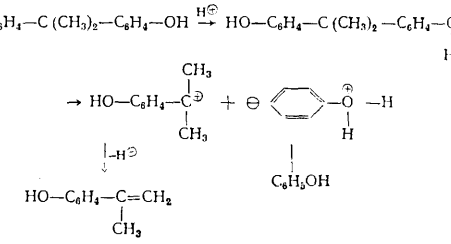
The decomposition of di(hydroxyphenyl)propane and its 2-alkyl derivatives at 170–235 °C *in vaçuo* (2–10 mmHg) in a stream of nitrogen or without it in the presence of NaOH, $Na_2CO_3$, or $CH_3COONa$ with simultaneous distillation of the decomposition products[29-31] leads mainly to phenol and p-isopropenylphenol, the yield of the latter being 90–98% of theoretical.

It is recommended that cracking of di(hydroxyphenyl)propane in the presence of sodium hydroxide be carried out at 120–180 °C and a residual pressure of 4 mmHg with two injections of alkali.[32] In this case up to 4% of p-isopropenylphenol dimer and trimer is formed together with phenol and p-isopropenylphenol.

The facilitation of the cracking of di(hydroxyphenyl)propane in the presence of alkaline and acid catalysts has been explained in different ways.[27] The hydroxy-group of one of the benzene rings gives rise to the bisphenol anion on treatment with alkali. The π electrons are then redistributed in the hydroxybenzene ring, as a result of which the bond between the central carbon atom and the second hydroxybenzene ring is broken:



When acids are used, the bond between the central carbon atom and the hydroxybenzene ring is weakened owing to the addition of the protons to one of the OH groups, which entails cleavage. The ions formed are stabilised by being converted respectively into p-isopropenylphenol and phenol:



The side products of the manufacture of di(hydroxyphenyl)propane can also be used to synthesise p-isopropenylphenol[33] but the yield of the desired product is low after their thermolysis. The method of synthesis of isopropenylphenol[34] by the thermal decomposition of p-isopropenylphenol

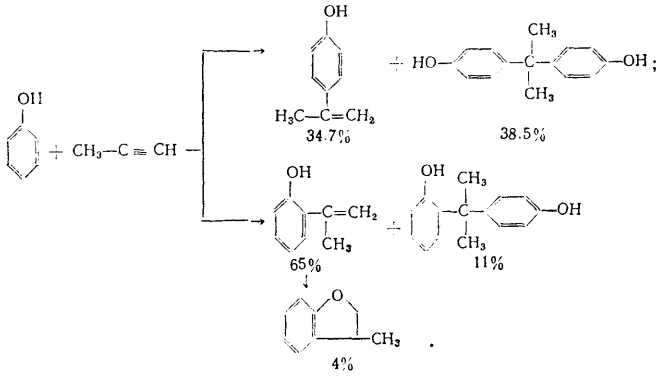
oligomers when these are injected continuously into an inert organic solvent heated to 150–250 °C at a pressure of 10 to 100 mmHg is of interest. *p*-Isopropenylphenol is obtained by this procedure in 98% yield and with a purity of 94.1%. The liquid-phase cracking of bis(4-hydroxyphenyl)alkanes or bis(4-hydroxyphenyl)cycloalkanes in the presence of a basic catalyst proceeds analogously.[35]

In order to prevent the dimerisation of *p*-isopropenylphenol, it is recommended that the vapour of the di(hydroxyphenyl)propane cracking product be irrigated with a polar solvent, for example with monohydric or dihydric alcohols; *p*-isopropenylphenol is isolated by diluting the alcoholic solution with water.[36]

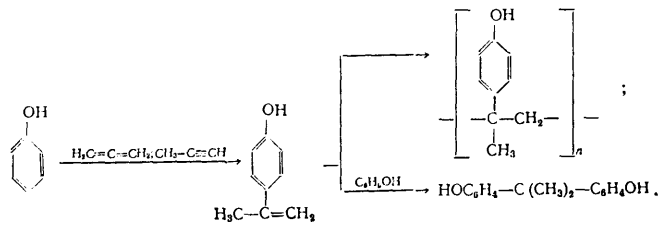
Overall, the cracking of di(hydroxyphenyl)propane in the presence of alkalis[26,29–31] ensures a fairly high yield (~90–98%) of the desired product—*p*-isopropenylphenol and its 2-alkyl derivatives. However, the main deficiency of this method involves the use of pure di(hydroxyphenyl)propane as the starting material which is at the present time a fairly expensive and scarce monomer, used in the manufacture of epoxy-resins. The high cost of di(hydroxyphenyl)propane is due to the complexity of the technology involved in its isolation in a pure form from condensation products and the labour involved in the utilisation of the waste produced.

All this makes the above method of synthesis of isopropenylphenol expensive, although in many instances it is nevertheless used to synthesise *p*-isopropenylphenol, a technically important product, despite being uneconomic.

The next group of methods, which makes it possible to obtain isopropenylphenols, is based on the alkenylation of aromatic hydroxy-compounds by substituted acetylenes.[37] Thus the alkylation of phenol by methylacetylene, phenylacetylene, and t-butylacetylene leads to the desired compounds. In this case of methylacetylene the reaction proceeds with formation of *p*- and *o*-isopropenylphenols, 2,2-di(4-hydroxyphenyl)propane, 2',4''-dihydroxy-2,2-diphenylpropane, and methylbenzofuran:




It is noteworthy that *p*-isopropenylphenol is also formed as an intermediate in the synthesis of di(hydroxyphenyl)propane by the reaction of phenol with allene or methylacetylene:[38]




Among other methods of synthesis of vinyl- and isopropenyl-phenols which are of industrial interest, mention may be made of the alkylation of phenol by ethylene and propene with subsequent dehydrogenation of ethyl- and isopropyl-phenols. The results of a study of the alkylation of phenol by ethylene and propene over aluminosilicates have been published;[39] the resulting mixtures of isomers of ethyl- and isopropyl-phenols were dehydrogenated in the presence of the "styrene-catalyst" (79.5% ZnO, 5.5% MgO, 5% $Al_2O_3$, 5% CaO, 2.5% $K_2SO_4$, and 2.5% $K_2Cr_2O_7$). The dehydrogenation of ethylphenols was accompanied in this instance by appreciable coke and gas formation; the yield of vinylphenols was low and their isolation in a pure form was difficult because of tar formation. The dehydrogenation of the mixture of isomeric isopropylphenols proceeds analogously.

When the *m*- and *p*-isomers of ethyl- and isopropyl-phenols are dehydrogenated in the presence of Cr–Al and magnesium, iron, copper, potassium, chromium, and tin oxides in the temperature range 400–700 °C, alkenylphenols are formed in yields of ~48–56%.[6,40,41] The dehydrogenation of isopropylphenols in the presence of catalysts such as the copper–chromium No.4 catalyst, the oxide No.40 catalyst, the "styrene-catalyst", and the "R-1" catalyst without and with a diluent ($CO_2$, $H_2O$) at 495–620 °C at atmostpheric pressure[39,42–45] gives rise to satisfactory yields of isopropenylphenol.

When $Fe_2O_3$ promoted by $K_2O$ is used as the catalyst, both on a carrier (alkaline earth metal oxides) and without a carrier, at 525 °C and a space velocity of 0.3 $h^{-1}$, the degree of conversion of *p*-ethylphenol is 8% and the selectivity of the formation of *p*-vinylphenol reaches 85%.[46]

The low yield of products, the intensified cracking, the charring of the initial alkylphenols, and rapid coke formation on the catalyst proved to be serious obstacles to further development of this extremely attractive, at first sight, method of synthesis of vinyl- and isopropenyl-phenols. Furthermore, the use of a mixture of isomers of the initial alkylphenols led to the formation of an extremely complex mixture of their dehydrogenation, cracking, and oligomerisation products, which hindered the isolation of the pure isomers of vinyl- and isopropenyl-phenols from it.

Other methods of synthesis of alkenylphenols have also been described in the literature. Thus 2,6-di-t-butyl-4-isopropenylphenol has been obtained in 70% yield by the reaction α-bromoisopropyl 3,5-di-t-butyl-4-hydroxyphenyl ketone with sodium hydroxide in an alcoholic solution.[47] A method of synthesis of *m*-isopropenylphenol by the acid decomposition of di-isopropylphenyl hydroperoxide with subsequent neutralisation of the reaction mixture and distillation in the presence of alkali (pH up to 9) has been proposed.[48]

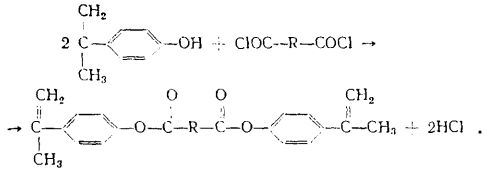
Thus one may conclude that, from the standpoint of its likely usefulness, the method involving the dehydrogenation of alkylphenols is of definite interest. However, the lack of effective catalysts precludes the wide-scale employment of this method in practice. We believe that the method based on the catalytic cracking of di(hydroxyphenyl)propane is most suitable at the present time. Here the yield of the desired product—*p*-isopropenylphenol—reaches 96% and above and the phenol formed as a side product is used to synthesise the initial di(hydroxyphenyl)propane.

## III. SYNTHESIS OF VINYLPHENOL ETHERS

The presence of the phenolic hydroxyl in vinylphenols retards their radical polymerisation compared with styrene. On converting them into their ethers, the capacity of the

ethylene bond for polymerisation increases significantly. The difference between the reactivities of the ethylene and ethyl groups makes it possible to carry out the oligomerisation or polymerisation of the vinylphenol ethers strictly via the ethylene group without involving the less reactive centres, which, forming part of the composition of the oligomers or polymers, are capable of subsequent participation in polymer-analogue transformations, imparting new practically important properties to the final polymeric product.

There is limited information in the literature, mainly in patents, about the synthesis of certain representatives of the ethers and esters of vinyl- and isopropenyl-phenols. Reactive monomers containing two isopropenyl groups in the molecule have been obtained[49] in yields up to 80% by the reaction of *p*-isopropenylphenol with the dichlorides of dibasic acids (carbonic, adipic, terephthalic, fumaric, etc.) in the presence of bases according to the scheme



The synthesis of *p*-isopropenylphenyl esters of acetic, propionic, benzoic, diethylphosphoric, and acrylic acids from their chlorides has been used as a classical method of organic chemistry, primarily to characterise chemically these individual compounds.[49-51] However, it was no less convenient to acylate the dimer or trimer of *p*-isopropenylphenol by acetic anhydride in the presence of acid catalysts with subsequent thermal or catalytic ($SiO_2$) decomposition of the di- and tri-acyl derivatives in order to obtain *p*-isopropenylphenyl acetate.[52] The initial dimers and trimers can be obtained by the cracking of di(hydroxyphenyl)propane in the presence of alkali. Among *p*-vinylphenol esters, 2,6-di-t-butyl-4-vinylphenyl acetate is known.[18,53] The silylation of *p*-vinylphenol by trialkylhalogenosilanes[54] and of 2,6-di-t-butyl-4-vinylphenol by *NN*-bis(trimethylsilyl)-acetamide has also been described.[18]

The synthesis of di[4-(*p*-isopropenylphenoxy)phenyl] sulphone by the reaction of *p*-isopropenylphenol with di(4-bromophenyl) sulphone in the presence of sodium hydroxide at 140 °C has also been described.[55] The yield of the desired product was 98.5%. The ethers of *p*-vinyl- and *p*-isopropenyl-phenols are usually obtained by the reaction of their phenoxides with the corresponding halogeno-derivatives.[56,57]

The methods of synthesis of the glycidyl ethers of vinyl- and isopropenylphenols are complicated by the dimerisation and polymerisation reactions of both the initial phenolic compounds and their glycidyl ethers. For this reason, the usual conditions for the preparation of the glycidyl ethers of phenols, alkylphenols, and allylphenols are unsuitable for the synthesis of the glycidyl ethers of vinyl- and isopropenylphenols. For example, a method of synthesis of the glycidyl ethers of allylphenol involving the gradual addition of a 40–60% aqueous solution of allylphenoxide (1 mole) to a boiling mixture of epichlorohydrin (2–2.1 moles) with benzene (1.1 mole) accompanied by the simultaneous azeotropic distillation of water has been described.[58] The yield of the glycidyl ether of allylphenol reaches under these conditions 95% relative to the allylphenol which has reacted. It has been shown that[59] under identical conditions the yield of the glycidyl ether of *p*-isopropenylphenol does not exceed 80%. This difference is explained in the first place by the characteristic features of the structures of aryl- and isopropenyl-phenols.

Whereas the ethylene bond in allylphenol is not conjugated with the benzene ring, in vinyl- and isopropenyl-phenols the conjugation of the ethylene bond with the aromatic system makes them more reactive and increases their tendency towards polymerisation. For this reason, when the glycidyl ether of *p*-vinylphenol is obtained from *p*-vinylphenol and epichlorohydrin in the presence of alkali, its yield does not exceed 11.1%.[60]

In order to suppress the polymerisation of vinyl- and isopropenyl-phenols and their glycidyl ethers, it is more useful to synthesise the latter in the presence of polymerisation inhibitors [1,4-di(2-naphthylamino)benzene and β-methyl-o-coumaric acid].[61] At the same time it has been recommended that the synthesis be performed in the presence of a large excess of epichlorohydrin and powdered alkali at 90 °C. However, even under these conditions, the yield of the desired product does not exceed 70% for the glycidyl ether of vinylphenol and 80% for the glycidyl ether of *p*-isopropenylphenol.

It is noteworthy that, under the conditions quoted above (elevated temperature, the presence of alkali and phenoxides in the reaction medium),[61] the epoxide ring of the resulting glycidyl ether is comparatively readily opened with an increase of the yield of side products.

The above data exhaust the available information about the synthesis of the glycidyl ethers of vinyl- and isopropenylphenols. Further studies on these lines should be directed towards finding conditions ensuring a high yield of the glycidyl ethers of vinyl- and isopropenyl-phenols and the suppression of the formation of side products. Much attention should be devoted in this connection to the simplification of the technology, a decrease of the consumption of energy and materials in the process, and the development of conditions for the isolation from the reaction products of the final ethers with a high purity and in high yields. Taking these requirements into account, the synthesis of glycidyl ethers of isopropenylphenols in a homogeneous medium at a low temperature (35–60 °C) using mono- or di-hydric $C_1$–$C_3$ alcohols as solvents has been investigated and developed recently. The yield of the desired product is 90–98%.[62]

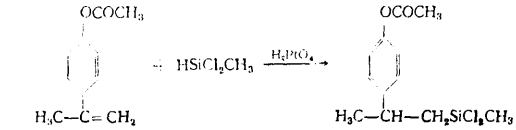
Thus the synthesis of only some esters and glycidyl ethers of vinyl- and isopropenyl-phenols has been described in the literature. These ethers and esters can be used for the modification of known polymeric materials and the synthesis of new ones. The development of convenient, waste-free methods of synthesis of the above monomers from readily available raw materials is therefore important.

The synthesis and study of the rearrangement of esters and allyl ethers of vinyl- and isopropenyl-phenols are of no less interest from the theoretical and practical points of view. Unfortunately the application of these reactions to the ethers and esters of vinyl- and isopropenyl-phenols has until recently been disregarded by investigators despite the abundance of studies on the Claisen rearrangement of allyl ethers[63-77] and the Fries rearrangement of esters[78-96] of phenols and alkylphenols.

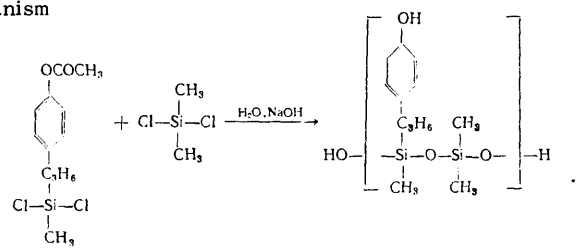
It was not until the 1980's that the first studies on the synthesis and then the photorearrangements and thermal rearrangements of allyl ethers of isopropenylphenols were published.[97,98] These investigations dealt with the reactions of *p*-isopropenylphenol and 2-alkyl-4-isopropenylphenols with allyl halides in acetone, alcohol, and water in the presence of alkali metal hydroxides and potassium carbonate. The conditions for the synthesis of new polyfunctional monomers—the allyl ethers of *p*-isopropenylphenol and 2-alkyl-4-isopropenylphenols in yields of 96.6 to 85%—have been elaborated (temperature 50 °C, *p*-isopropenylphenol : allyl halide molar ratio 1 : 4). It was shown

that the allyl ether of *p*-isopropenylphenol undergoes mainly the Claisen rearrangement both on heating (180 to 240 °C) and on exposure to UV light, with formation of a new polyfunctional monomer—2-allyl-4-isopropenylphenol in 95% yield.

The products of the hydrosilylation of *p*-isopropenylphenyl acetate at the double bond are of independent interest:[99]



The silyl derivative [2-(4-acetoxyphenyl)propyl]dichloromethylsilane can be used as the starting material in the synthesis of hydroxyphenylsiloxanes[99] in accordance with the mechanism

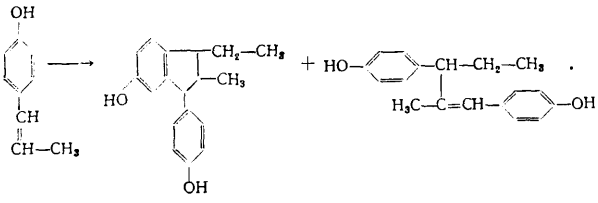


The oligosiloxanes obtained are readily hardened in the presence of hardening agents by a mechanism similar to that of the hardening of phenolformaldehyde oligomers of the novolac type.[100]

## IV. OLIGOMERISATION, POLYMERISATION, AND COPOLYMERISATION OF VINYLPHENOLS AND THEIR DERIVATIVES

Studies devoted to the oligomerisation, polymerisation, and copolymerisation of vinylphenols and their derivatives are of definite practical interest.

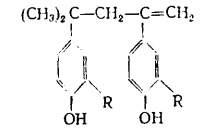
These monomers usually readily dimerise despite the possibility of the inhibiting effect of the phenolic hydroxyl. For example, the spontaneous dimerisation of *p*-propenylphenol (anol) on storage[101] is accompanied by the formation of a product referred to conventionally as "polyanol", which is a synthetic analogue of a female sex hormone:[102]



Vinylphenols readily dimerise and trimerise on heating and also in the presence of acid catalysts.[103–105] The following catalysts have been proposed for the dimerisation of isopropenylphenols (especially the *m*-isomer):[105] $H_2SO_4$, $AlCl_3$, $PCl_3$, $C_6H_5SO_3H$, $ClCH_2COOH$, $SnCl_4$, and $BF_3 \cdot O(C_2H_5)_2$. The dimerisation takes place at 110–130 °C. The dimer obtained can be isolated by vacuum distillation. The crystalline dimer is used to synthesise epoxy-resins or novolac resins.[105]

The solid-phase oligomerisation of *p*-isopropenylphenol under UV- or γ-irradiation leads to a low yield (5–10%) of oligomers with a molecular weight of 500–700.[106]

The dimers of *p*-isopropenylphenol and its alkyl derivatives,



where R is a halogen or an alkyl group, as well as their hydrogenation products react with phosgene to form thermoplastic polycarbonates having the general formula $-[-C(O)O-X-O-]_n$, where X is a residue of the dimer or the hydrogenated dimer.[107]

The dimerisation of *p*- and *o*-isopropenylphenols leads to the formation of the following linear and cyclic dimers: 2,4-di(4-hydroxyphenyl)-4-methylpent-2-ene, 2,4-di(4-hydroxyphenyl)-4-methylpent-1-ene, 2,4-di(2-hydroxyphenyl)-4-methylpent-1-ene, 2,4-di(2-hydroxyphenyl)-4-methylpent-2-ene, 1-(4-hydroxyphenyl)-1,3,3-trimethyl-6-indanol, and 2-hydroxy-2,4,4-trimethylflavan.[23]

Linear *p*-isopropenylphenol dimers are obtained in high yields on cracking di(hydroxyphenyl)propane in the presence of alkali.[108] They can serve as starting materials for the synthesis of thermoplastic and thermoreactive compositions. In particular, *p*-isopropenylphenol dimers are used for the modification of phenolic and alkyd resins.[109]

A mixture of dimers, trimers, tetramers, and other oligomers can be obtained by the oligomerisation of *m*-isopropenylphenol in the presence of acids or without them at 135–230 °C. The mixture contains about 50% of dimers and 30% of trimers.[110] $BF_3$ and alkylbenzenesulphonic acids have also been recommended as oligomerisation catalysts. Mainly tri-, tetra-, penta-, and hexa-mers, used in the manufacture of novolac epoxy-resins with increased mechanical strength, are formed in their presence at temperatures below 20 °C.[111,112]

Linear trimers of *p*-isopropenylphenol have been obtained by the depolymerisation of its linear polymers and also of a mixture of the *p*-isopropenylphenol dimer and polymer in an organic solvent and in the presence of acid catalysts at 0–100 °C.[113,114] These trimers are used in the synthesis of thermoreactive resins and as vulcanising agents for epoxy-resins.

In order to synthesise *p*-isopropenylphenol oligomers with a molecular weight of 500–600, it is best to polymerise the phenol in the presence of iodine in benzene at 30 °C. After 40 h, the degree of conversion of *p*-isopropenylphenol reaches 79.3%.[115] The oligomers obtained can be used in adhesive compositions and in the preparation of ion-exchange resins and high-molecular-weight water-soluble compounds.

In order to obtain polymers with a relatively low molecular weight, isopropenylphenol can be introduced into a preliminary reaction with maleic anhydride[116] and other unsaturated compounds. Propenylphenol reacts analogously with maleic anhydride.[117] Thus, on condensation with maleic anhydride, *o*-propenylphenol gives rise to an adduct with m.p. 308 to 312 °C, which is soluble in alcohol. Under the same conditions, *p*-propenylphenol gives rise to a readily separable product with m.p. 113–114 °C, which has been identified as the *p*-propenylphenyl monoester of maleic acid.[117]

*p*-Isopropenylphenol and its oligomers are used to synthesise modified phenolformaldehyde resins employed in the manufacture of laminated plastics. For this purpose, *p*-isopropenylphenol and its oligomers are first condensed with unsaturated oils of plant origin and the products obtained, mixed with other phenolic compounds, are then condensed with formaldehyde.[118–128]

Compositions based on *p*-isopropenyl derivatives (consisting of *p*-isopropenylphenol and its oligomers) and compounds in the group of linear unsaturated acids, fats and oils, polydienes, and the products of their "maleic treatment" are used as corrosion- and water-resistant coatings.[115]

Questions concerning the homopolymerisation of vinylphenol are of interest. Specific attention has also been devoted to this problem in the literature. The polymerisation of *p*-vinylphenol has been investigated in the presence of radical initiators and cationic and anionic catalysts with formation of oligomers.[53] In order to synthesise polyvinylphenol, it is necessary to carry out the preliminary polymerisation of *p*-vinylphenyl acetate with subsequent hydrolysis of the resulting poly(*p*-vinylphenyl acetate) with a 10% sodium hydroxide solution containing 5–10% of alcohol. The glass point of the polyvinylphenol formed is 170–180 °C.

The polymerisation of 2-methoxy-4-vinylphenol in an atmosphere of nitrogen in the dark gave rise to di-, tri, and tetra-mers and oligomers with $n > 4$ in yields of 33, 13.4, 11, and 42.6% respectively. It has been shown[130] that, in the presence of azobisisobutyronitrile, the polymerisation reaction is of first order with respect to the initiator; it has been suggested that the oligomer is formed via a cationic mechanism as a consequence of the influence of the acidic phenolic hydroxyl.

The radical polymerisation of vinylphenol in the presence of atmospheric oxygen leads to the formation of dark-coloured polymers.[131] For the preparation of colourless polyvinylphenols, it is recommended that the process be performed in the absence of oxygen.[132] The colourless polyvinylphenols obtained are suitable for esterification [etherification?] and the formation of moulding powders and varnishes.

Poly-*p*-vinylphenol is also readily cross-linked by formaldehyde and hexamethylenetetramine, forming thin films.[133]

The polymerisation of *p*-vinylphenol has also been investigated in the presence of $BF_3.O(C_2H_5)_2$, $BF_3$, $AlCl_3$, $SnCl_4$, $VOCl_3$, $Al(C_2H_5)_2Cl$, etc. in aliphatic or aromatic nitriles and methylene chloride. The molecular weight of the poly-*p*-vinylphenol obtained reaches 116000–530000 and the use of nitriles as solvents makes it possible to obtain polymers with the maximum molecular weight.[134,135]

A poly-*p*-vinylphenol with a comparatively low molecular weight (7000) can be obtained by polymerising *p*-vinylphenol in the presence of $P_2O_5$, HF, $H_2SO_4$, $H_3PO_4$, HCl, and boron, antimony, iron, tellurium, tin, titanium, bismuth, and indium halides.[136,137]

Comparative differential thermal analysis of polystyrene, poly-*p*-vinylphenol, poly-3-methoxy-4-vinylphenol, and their acetates has shown[138] that all the specimens investigated are stable up to 297–327 °C and that the above polymers have the same temperatures of the onset of degradation as polystyrene. The activation energy for the decomposition of poly-*p*-vinylphenyl acetate is highest (70 kcal $mol^{-1}$) and that for the decomposition of poly-*p*-vinylphenol is lowest (40 kcal $mol^{-1}$). The activation energy for the decomposition of poly-3-methoxy-4-vinylphenol is 53 kcal $mol^{-1}$. The glass point increases by 10–50 °C after the introduction of the OH and $CH_3-\overset{O}{\overset{\|}{C}}-O$ groups in the *p*-position in the benzene ring relative to the polymer chain, while the introduction of the $CH_3-\overset{O}{\overset{\|}{C}}-O$ group in the *m*-position entails a decrease of the glass point. This difference between the glass points can be accounted for by the presence of hydrogen bonds and the limitation of molecular mobility in poly-*p*-vinylphenol.[138]

A phosphorus-containing poly-*p*-vinylphenol has been synthesised by the reaction of brominated poly-*p*-vinylphenol with $P(OCH_3)_3$.[139] The resulting phosphorus-containing polymer is used to impart fire resistance to thermoplastic and thermoreactive polymer compositions.

Poly-*p*-vinylphenol is used in polymer compositions for adhesives, hermetic seals, and cross-linking agents and also in the manufacture of laminated and moulded materials.[140]

Polyvinylphenol has been manufactured in the USA under the commercial names Resin-M and Resin-MB under a Japanese licence with an annual production of 100 tonnes. These linear high-molecular-weight powders have found extensive applications as hardening agents, light-sensitive materials, combustion inhibitors, and agents imparting electrical conductivity.[141]

The copolymerisation of vinylphenol with different monomers has also been investigated. Thus copolymerisation with butadiene, isoprene, and chloroprene in emulsion, in bulk,[142] and in solution[143] in the absence of oxygen leads to the formation of light-coloured copolymers capable of being vulcanised via the residual double bonds or via a polycondensation reaction with aldehydes. Such copolymers are suitable for use in casting compositions and varnishes and as cross-linking components.

The synthesis of the copolymers of vinylphenols with cyclopentadiene in the presence of $H_2SO_4$, HCl, $SnCl_2$, $BF_3$, $POCl_3$, and $BF_3.O(C_2H_5)_2$ has been described.[144,145] The possibility of using organic peroxides as the initiators of this reaction has also been demonstrated,[122] but these proved to be less effective. The radical copolymerisation of benzyl methacrylate with the phenyl ether of *p*-vinylphenol has been studied[146] and the copolymerisation constant has been determined. In order to obtain a thermoreactive product resistant to water, alkali, and acid, it is recommended that vinylphenol be copolymerised with styrene, methylstyrene, acrylic derivatives, *N*-vinylpiperidine, and allyl derivatives with subsequent treatment of the resulting copolymers with aldehydes in an alcoholic alkaline medium.[147]

Studies[148] on the polymerisation and copolymerisation of 2,6-di-t-butyl derivatives of *p*-vinylphenol, *p*-isopropenylphenol, and *p*-isopropenylanisole with styrene showed that the last two monomers readily polymerise and copolymerise in the presence of $BF_3.O(C_2H_5)_2$, $TiCl_4$, and $Al(C_2H_5)_3$, forming polymers and copolymers with molecular weights of 3900 to 15000. Depending on the monomer ratio, soluble, partly soluble, and completely insoluble copolymers are obtained with styrene or α-methylstyrene. The yield of the polymers (copolymers) varies from 1 to 37%. The copolymerisation constants have been determined for the following pairs of monomers: 2,6-di-t-butyl-4-vinylphenol ($r_1 = 3.4$) and styrene ($r_2 = 0.046$); 2,6-di-t-butyl-4-isopropenylphenol ($r_1 = 1$) and styrene ($r_2 = 0.076$). The copolymerisation of 2,6-di-t-butyl-4-vinylphenol (10.5%) with ethylene or propene (89.5%) in the presence of $TiCl_4$ and $Al(C_2H_5)_3$ gives rise to soluble copolymers.

The copolymers of vinyl- and isopropenyl-phenols with aromatic vinyl monomers have been recommended[149,150] as hardening agents for epoxy-resins (in combination with anhydride hardening agents). The hardened compositions are characterised by an improved mechanical strength, thermal stability, dielectric properties, and resistance to the action of moisture and alkalis.

The copolymerisation of 2-methoxy-4-vinylphenol with fluorinated acrylic monomers in acetone at 60 °C in the presence of azobisisobutyronitrile makes it possible to obtain copolymers characterised by an enhanced resistance to water and oil.[151]

Vinylphenol polymers and copolymers can also be obtained using various vinylphenol ethers. An interesting method of synthesis of ion-exchange resins capable of chelate formation has been described in a British patent.[152] In this case

the vinylphenol ester (*p*-vinylphenyl acetate) copolymerises with divinyl compounds (divinylbenzene, divinyl ether, etc.). The product obtained is hydrolysed and the $NO_2$, $NH_2$, COOH, $SO_3H$, $CH_2Cl_2$ etc. functional groups are introduced into the "cross-linked" polyvinylphenols formed.

The "cross-linked" polyvinylphenols containing the AsO.$(OH)_2$ groups in the benzene ring, obtained by the reaction of the "cross-linked" polyvinylphenol with diazotised arsenilic acid or by diazotising polyvinylaminophenol and subsequent treatment with sodium arsenite, can be used to extract uranium from dilute solutions.[153]

The polymerisation of the glycidyl ether *p*-vinylphenol in bulk leads to a resin with an intrinsic viscosity of 0.81 dl $g^{-1}$ (in dioxan at 30 °C).[60] The glycidyl ether of *p*-vinylphenol and its polymer are used in the making of cast articles.

Soluble polymers have been obtained by polymerising the allyl ethers of *o*- and *p*-vinylphenols in the presence of $BF_3.O(C_2H_5)_2$ or benzoyl peroxide.[154] The polymerisation in the presence of azobisisobutyronitrile in dilute solution results in the formation of a soluble polymer, while in a concentrated solution the product is an insoluble polymer with cross links. The copolymerisation of these monomers with ethyl vinyl ether and styrene has also been carried out successfully using $BF_3.O(C_2H_5)_2$ as the catalyst. The Claisen rearrangement, cross linking induced by radical initiators, and the formation of epoxides on treatment with $C_6H_5COOOH$ are also possible for polymers obtained by the polymerisation of the allyl ether of *p*-vinylphenol.[154]

The copolymers of vinylphenols also serve as the starting materials for the synthesis of carriers for the catalysts of the oligomerisation of unsaturated hydrocarbons. Thus polymeric carriers with a high swellability in hydrocarbon solvents, a reduced hygroscopicity, and an increased stability have been obtained[155] by using tervalent phosphorus compounds to treat hydroxyl-containing copolymers of styrene with vinylphenols or their glycidyl ethers in organic solvents at 20–110 °C. The carriers obtained contain groups capable of forming complexes with a transition metal compound, in which the central atom is either coordination unsaturated or is bound to other mobile ligands which are readily displaced.

The polymerisation and copolymerisation reactions of isopropenyl- and propenylphenols have been investigated to a much lesser extent than those of vinylphenols. Thus a study has been made[156] of the copolymerisation of *p*-isopropenylphenol (PIP) with butadiene, isoprene, vinyl acetate, and methyl methacrylate, acrylonitrile, methyl acrylate, ethyl acrylate, and styrene in the presence of azobisisobutryronitrile at 60 °C. High-molecular-weight copolymers are not obtained with butadiene, isoprene and vinyl acetate. In the remaining cases the products are copolymers with molecular weights in the range 8000–50000. The reactions of *p*-isopropenylphenol with acrylonitrile and methyl acrylate give rise to alternating copolymers. In all cases an increase in the mole fraction of *p*-isopropenylphenol in the mixture of monomers entails a fall in the rate of copolymerisation. The comonomers can be arranged in the following sequence in terms of the reactivities: acrylonitrile > methyl acrylate > ethyl acrylate > methyl methacrylate. For each PIP–acrylonitrile, PIP–methyl acrylate, and PIP–ethyl acrylate pair, the copolymerisation constants $r_1$ and $r_2$ have been determined as 0.07 and 0.02, 0.28 and 0.12, and 0.65 and 0.92 respectively.

A method of synthesis of copolymers of *p*-isopropenylphenol with styrene in acrylonitrile in solution using as catalysts Lewis acids, for example $AlCl_3$, and $ZnCl_2$ or even inorganic acids ($H_2SO_4$) in an amount of 0.001–5% of the weight of the monomers has been described.[157] The copolymers have a molecular weight of 500–2000 and are readily soluble in many organic solvents and solutions of alkalis. They are suitable for the manufacture of varnishes and plastics.

The reactivity of *p*-isopropenyl phenylacetate in the free radical copolymerisation with butadiene has been estimated.[158,159] The constants for the copolymerisation of *p*-isopropenylphenyl acetate with butadiene were determined in this instance spectrophotometrically and radiometrically (at 60–80 °C). The activity factors $Q$ and $e$ have been calculated for *p*-isopropenylphenyl acetate.

A method for the synthesis of the copolymer of *o*- or *p*-isopropenylphenol 2-alkyl-4-isopropenylphenols with styrene, maleic anhydride, and acrylonitrile in the presence of t-butylperoxide (TBP) and azobisisobutyronitrile (AIBN) has been described.[160,161] For a 1:1 ratio of the isopropenylphenol and maleic anhydride and a 1:2 ratio of isopropenylphenol and acrylonitrile (at 80° and 140 °C), the yields of the copolymers were 37–49% and 92–96% respectively.

The co-oligomerisation of 1–30% of *p*-isopropenylphenol with 70–99% of styrene in the presence of 0.1–0.2% of TBP at 140 °C is completed in 30 h. The yield of the co-oligomers is 93–99%. An increase in the amount of isopropenylphenol in the initial mixture of monomers lowers the rate of copolymerisation and leads to the formation of copolymers with reduced softening temperatures and intrinsic viscosities.

One of the promising applications of the co-oligomers of isopropenylphenols with styrene, maleic anhydride, and acrylonitrile involves their use as hardening agents for industrial epoxydian resins.† The phenolic hydroxyl and the anhydride group in the co-oligomers readily react with the epoxide ring and the OH group of the epoxydian resin, such interaction resulting in a hardening product with an improved heat resistance, adhesive strength, etc.[149].

The allyl ether of *p*-isopropenylphenol copolymerises readily with styrene in bulk and in solution (in ethylbenzene) in the presence of TBP as the initiator.[162] The copolymerisation in bulk is complicated by the formation of a gel-fraction, whose yield increases with temperature and with the amounts of the allyl ether of *p*-isopropenylphenol and the initiator in the initial mixture of monomers. The copolymerisation in ethylbenzene proceeds smoothly with virtually total conversion of the monomers. In the co-oligomerisation in solution, the ethylene bond of the isopropenyl group is more reactive than that in the allyloxy-group, as a result of which the selective synthesis of co-oligomers containing reactive allyloxy-groups becomes possible.[163,164] Studies on the characteristic features of the thermal structure formation in the co-oligomers containing 10, 20, and 30% of units comprising the allyl ether of *p*-isopropenylphenol have shown that their thermal hardening at 180–240 °C proceeds with the opening of the ethylene bond in the allyl group. Coatings based on the above copolymers have improved UV- and thermo-oxidative resistances, adhesive and impact strengths, and elasticities.

The copolymerisation of the glycidyl ether of *p*-isopropenylphenol with styrene and acrylonitrile in bulk in the presence of TBP and AIBN has been studied.[165] The copolymerisation constants for the copolymer of styrene ($r_1$) and the glycidyl ether of *p*-isopropenylphenol ($r_2$) are $r_1 = 2.42 \pm 0.78$ and $r_2 \cong 0$.

The copolymers of the glycidyl ether of *p*-isopropenylphenol with styrene are readily hardened by polyethylenepolyamine, *p*-phenylenediamine, and maleic and phthalic anhydrides and also thermally and on irradiation with UV

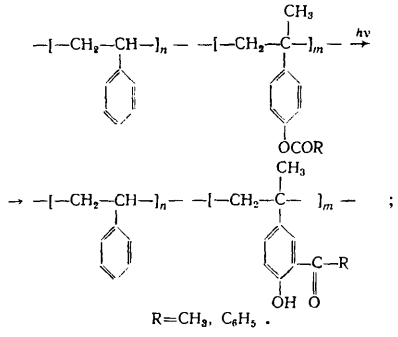
†Dian = 2,2-di(4-hydroxyphenyl)propane (Ed.of Translation).

light. The loss of weight by the "cross-linked" copolymers at 250 °C over a period of 24 h depends on the composition of the product and varies in the range 10–30% (38–40% for polystyrene).[166]

When the co-oligomers of *p*-isopropenylphenol or 4-isopropenyl-2-methylphenol with styrene and acrylonitrile were allowed to react with epichlorohydrin, a reactive oligomer containing simultaneously an epoxide ring and a phenolic hydroxyl was obtained.[167]

The heat resistance and thermal stability of the above plastics can be improved in introducing units comprising the glycidyl ethers of isopropenylphenols into the polystyrene chain with their subsequent thermal hardening. The glycidyl ether of *p*-isopropenylphenol co-oligomerises effectively with maleic anhydride and styrene in the presence of the AIBN initiator and in its absence.[168] The co-oligomerisation of the glycidyl ether of *p*-isopropenylphenol with maleic anhydride (1 : 1) and a mixture of maleic anhydride and styrene (1 : 2 : 1) both in bulk and in solution (in ketones) at 60 °C proceeds with intermediate formation of a charge-transfer complex and leads to the formation of binary and ternary co-oligomers with alternating monomer units respectively. These co-oligomers are readily hardened in the presence of moisture and also amines at 100–180 °C with the opening of the anhydride and epoxy-groups present in the co-oligomer. Coatings based on these co-oligomers are characterised, before and after hardening respectively, by impact strengths of 10 and 50 kg(force) $cm^{-2}$, elasticities of 1 and 10 mm, hardnesses of 0.72 and 0.9, and adhesive strengths of 4.0 and 89.9 kg(force) $cm^{-2}$.

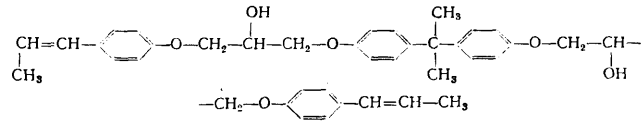
The results for the copolymerisation of p-isopropenylphenyl acetate and *p*-isopropenylphenyl benzoate with styrene in bulk in the presence of TBP have been published.[169] Under the influence of UV light, the Fries rearrangement takes place in *p*-isopropenylphenyl ester units of the polymer chain with formation of hydroxyacetophenone and hydroxybenzophenone groups, which improve the photostability of the copolymers:



R=$CH_3$, $C_6H_5$ .

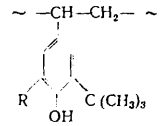
A method for the modification of the p-isopropenylphenol–styrene copolymer (hydroxyl index 112–116) by the glycidyl ether of *p*-isopropenylphenol in the presence of sodium hydroxide is also known.[170] The yellow modified resin softens at 85 °C and is soluble in the majority of organic solvents. Di(isopropenylphenyl) ether has also been recommended as a modifying comonomer for the modification of properties, especially for improving the heat resistance of polystyrene.[171] It has also been suggested[172] that the linear *p*-isopropenylphenol homopolymer and epoxy-resins be used for the preparation of thermoreactive polymeric materials with high heat and chemical resistances.

A method of synthesis of "cross-linked" copolymers (Marten heat resistance 87°, Dinstat [DIN static bending test? (Ed.of Translation)] bending strength 976 kg $cm^{-2}$, specific impact strength 4.3 kg $cm^{-2}$, and hardness 1415 kg $cm^{-2}$) by the copolymerisation of ~95% of a vinyl monomer (for example, styrene) with 5% of a tetrafunctional monomer, obtained by the reaction of 2 moles of the glycidyl ether of *p*-propenylphenol with 1 mole of bisphenol, has been proposed in a patent:[173]



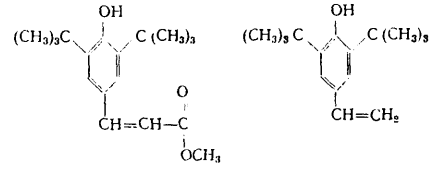
Shielded derivatives of vinylphenols, in particular 2,6-di-t-butyl-4-vinylphenol and 2,6-di-t-butyl-4-isopropenylphenol, are of interest for the synthesis of high-molecular-weight anti-oxidants by their copolymerisation with other monomers.[174] The dimers of 2,6-dialkyl-4-isopropenylphenols and their salts can also be used as anti-oxidants in rubbers and oils.[175]

A composition with an improved resistance to the action of oxidants has been obtained on the basis of polypropylene and poly-t-butyl-p-vinylphenol.[176]



R = H, t-butyl.

In order to improve the stability of the polymers of styrenes, vinyl acetate, vinyl chloride, ethyl acrylate, acrylonitrile, and butadiene, it has been suggested that[177] the latter be copolymerised with unsaturated sterically hindered phenols:



The reactions are carried out under a high pressure in the presence of 0.5% of AIBN in solution in toluene. The phenolic compounds are used in amounts of ~3%.

## V. POLYCONDENSATION OF VINYLPHENOLS WITH ALDEHYDES

In contrast to phenol- or alkylphenol-aldehyde resins, alkenylphenolaldehyde resins are capable of being hardened via the alkenyl groups with the evolution of little or no volatile products. Furthermore, they can be structured by vinyl monomers with formation of "cross-linked" copolymers with improved water resistance, chemical resistance, and dielectric properties. Allylphenolformaldehyde resins also have similar properties. Thus allylphenolformaldehyde resins capable of being thermally hardened at 180–250 °C have been obtained by the allylation of a novolac phenol-formaldehyde resin and the polymerisation of the allyl ether of 2,6-dihydroxymethyl-*p*-cresol with subsequent thermal rearrangement of polyallyl ethers.[178–180] The cross-linking of allylphenolformaldehyde resins has also been investigated using cross-linking monomers (styrene, α-methylstyrene, acrylonitrile, and 2-methyl-4-vinylpyridine) in the presence of cationic catalysts.[180] It was shown that the copolymerisation of the allyl ether of novolac in the presence of cationic catalysts proceeds smoothly and at a fairly high rate, while the reaction initiated by free radicals either does not occur or is characterised by a low extent of completion.

Polycondensation resins have also been synthesised using *o*-allylphenol,[126] *trans*-hydroxymethylphenylallyl ether,[181] and cardanol (a monohydric phenol with a $C_{15}$ side chain, containing double bonds, in the *meta*-position) obtained by the distillation of the oil from the seeds of *Anacardium occidentale*.[182]

Allylic resins possess a high thermal stability and moisture and chemical resistances as well as a low toxicity and are used as laminate and moulding materials and also in the form of varnish coatings.[183,184]

In contrast to allylphenolformaldehyde resins, vinyl- and isopropenyl-phenolformaldehyde resins are readily hardened via a free-radical mechanism at lower temperatures.

A method of synthesis of vinyl- and isopropenyl-phenolformaldehyde resins by the polycondensation of *m*-vinylphenol and *o*- and *p*-isopropenylphenols with formaldehyde has been described.[185-187] The unsaturated resin obtained can be readily hardened and can be used in oil-based insulating varnishes and for the preparation of moulding powders and adhesives.

A resin with improved flexibility (without impairment of its electrical properties), thermal stability, chemical resistance, and size stability has been obtained by the polycondensation of *p*-isopropenylphenol and its oligomer with formaldehyde in the presence of an acid catalyst; this resin is used as a binder in the manufacture of electrically insulating laminate materials.[188]

The condensation of *p*-isopropenylphenol or its dimer with formaldehyde can take place in the presence of bases,[189] for example, 28% of an aqueous solution of ammonia at 95 °C. The laminate plastic obtained using the resin thus synthesised is characterised by higher bulk and surface resistivities ($4.5 \times 10^{12}$) compared with the usual phenolformaldehyde resin ($10^9$–$10^{10}$).

These studies exhaust the available literature data on the polycondensation of vinyl- and isopropenyl-phenolformaldehyde resins. Thus the existing possibilities for the synthesis of alkenylphenolformaldehyde resins by the polycondensation reactions have so far been by no means fully utilised. The synthesis of *p*-alkylphenolformaldehyde and ureaformaldehyde resins modified by vinyl- and isopropenylphenols is also of theoretical and practical interest.

The literature data described above permit the conclusion that the chemistry of vinyl- and isopropenyl-phenols has developed vigorously in recent years both in the direction of the creation of effective processes for their synthesis and of the study of their oligomerisation, homopolymerisation, copolymerisation, and polycondensation. Taking into account the differences between the reactivities of the ethylene bond, the phenolic hydroxyl, and the ether and other functional groups, definite advances have been made in the synthesis of new and the modification of existing oligomers and polymers using these polyfunctional monomers. Particular mention should be made of the advances in the creation of unsaturated phenolformaldehyde oligomers, which are hardened without the evolution of volatile products, self-stabilising copolymers, and new composite materials characterised by improved physicochemical and dielectric properties.

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# Intermolecular Interaction in Solutions of Graft Copolymers

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Experimental data for the intermolecular interaction in block and graft copolymers and also the relation between their molecular structure and the properties of their solutions are examined systematically and critically. Problems concerning micelle formation, the microstructure, the conformation, and especially the thermodynamic properties of solutions of graft copolymers are described and the characteristic features of the influence of individual factors on the properties of solutions of graft copolymers are discussed.
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## I. INTRODUCTION

The macromolecules of graft copolymers consisting of two or more polymeric sections of different nature, linked chemically to one another, are branched, in contrast to the statistical and block copolymers which have a linear structure. The combination of the properties of several macromolecular compounds in graft copolymers is determined by the specific features of their molecular structure. The properties of graft copolymers are determined by the number and molecular weight of the grafted branches, the molecular weight of the main chain, their molecular weight distribution, and the inhomogeneity of the composition of the macromolecules, and also the nature of the main chain and the grafted branches, the degree of their compatibility, and the conformations of the macromolecules in the solvents employed. By altering the parameters enumerated above, it is possible to regulate the molecular and supermolecular structures and to impart to them the necessary properties. Graft copolymers have found industrial applications as impact resistant thermoelastic plastics, polymeric emulsifying agents, stabilisers for multicomponent polymer systems, membranes for reverse osmosis, etc. The two-phase structure of the polymers, caused by the separation of the microphases of the incompatible components into distinct domains (in the solid state), plays a significant role in the development of such products. The degree and nature of such separation depend on many factors, which were enumerated above. Numerous studies of the characteristic features of the formation of the two-phase structure of block copolymers, the ease of formation of which is determined by the linear structure of the macromolecules, have been described in the literature.

Studies of the macromolecular interaction in ternary systems have been analysed[1-5] and a number of communications have been devoted to different aspects of the intermolecular interaction in polymer blends.[6-20] The literature data on the microphase separation in block copolymers and the influence of various factors on their properties in solution and in the solid state have been analysed;[1,21] in addition reviews and monographs have been published.[22-34] The available literature data on the macromolecular interaction in graft copolymers require a systematic treatment and need to be surveyed. On the other hand, new studies on block copolymers, which also need to be surveyed, have been published in recent years.

## II. MICROPHASE SEPARATION IN MULTICOMPONENT SYSTEMS

Numerous publications on studies of the structure of block copolymers[1,21,22,25,29] permit the conclusion that the incompatibility of the blocks in block copolymers promotes phase separation. This leads in its turn to the formation of microdomains, which are arranged regularly in space and form mesophases in the presence of a solvent. It has been noted[22,26] that the best methods for the investigation of such systems are low-angle X-ray scattering and electron microscopy, which have shown that the microdomains have the form of either lamellae, or cylinders, or spheres. The same conclusions concerning the phase separation of block copolymers have been reached by investigators who studied microphase separation by thermomechanical,[35-40] scanning calorimetric,[41,42] and sorption[43-45] methods. Investigation of the influence of the molecular structure of the block copolymer on the microphase separation have shown that, for the same molecular weight of the block copolymer, an increase in the number of blocks hinders separation into layers[35] and that the critical parameter of the interaction between blocks in "star-shaped" block copolymers is lower than for linear block copolymers.[46]

Since the microphase separation process begins to be manifested at the molecular level, the question of the dependence of the conformation of the macromolecule on the segregation factor $\chi_{AB}$, which determines both the formation and the stability of the supercrystals, becomes significant.[8] In dilute solutions of block and graft copolymers the use of selective solvents or the addition of a precipitant to a copolymer solution causes the formation of micelles at the molecular level as a consequence of the intramolecular "precipitation" of the insoluble components. Different forms of the macromolecular micelles of block and graft copolymers in dilute and concentrated solutions have been described.[1,21,22] The characteristics of the formation of

monomolecular and polymolecular micelles from block and graft copolymers have been discussed and the influence of various factors on the micelle formation process has been examined in a number of investigations.[25,26,32-34,47-54]

The literature data on the micelle formation in block and graft copolymers do not provide an answer to the question how the molecular weight of the blocks or grafted branches influences the formation of monomolecular or polymolecular micelles. However, it has been noted that, as the number of block or grafted branches increases, only monomolecular micelles can be formed in solutions of copolymers, because a large number of block or grafted branches protects the nucleus of the micelle, which hinders the formation of polymolecular micelles. The nature of the solvent also influences the formation of micelles: in solvents which are "good" for both components of the copolymer, the microphase separation is impaired, while in selective solvents the heterocontacts between unlike segments are reduced to a minimum and the possibility of the formation of monomolecular or polymolecular micelles is sharply increased. These data confirm the finding that, with increase in the difference between the parameters of the thermodynamic interaction of the components of the copolymer with the solvent $\chi_{12} - \chi_{13} = \Delta\chi$ (the "$\Delta\chi$ effect"), the compability of the components is impaired, which leads to microphase separation in the copolymers and the formation of micelles.

Micelle formation by the macromolecules of block and graft copolymers is a very important factor, since, by using different solvent–precipitant systems, it is possible to regulate the type of micelle, which enables one to obtain "hard" or "soft" forms of the polymer.[21,22] Concentrated solutions of block copolymers form ordered mesomorphic phases resembling lyotropic liquid crystals. In reality these microheterogeneous highly ordered segregated domains, made up of blocks of one type, are typical of supercrystals.[1,8,21]

## III. CHARACTERISTICS OF THE BEHAVIOUR OF GRAFT COPOLYMERS IN SOLUTION

In contrast to block copolymers, graft copolymers do not tend to form supercrystals owing to the branched structure of their macromolecules and steric hindrance. However, despite the branched macromolecular structure of copolymers, the possibility of the formation of highly organised structures of the type of dendrites as a consequence of strong specific interactions of the solvent with the grafted component via hydrogen bonding, leading to the unwinding of the grafted branches and the establishment of a definite order in the latter, has been demonstrated.[55]

It has been shown for graft poly(vinyl alcohol)–poly-2-vinylpyridine (PVA–P-2-VP), cellulose diacetate–polyacrylamide (CDA–PAA), and cellulose diacetate–poly-2-vinylpyridine (CDA–P-2-VP) graft copolymers[55-57] that an increase in the strength of donor–acceptor interactions of acetic acid molecules with PAA and P-2-VP chains causes the formation of structures of the "fern leaf" type with a distinct centre of growth, which become more ideal with increase in the content of the grafted polymer. This phenomenon is encountered fairly rarely for amorphous graft copolymers, because, under the usual conditions, the crystallisation of CDA is hindered by the breakdown of the regularity of the chain structure when some of the acetate groups are replaced by hydroxy-groups.

When solutions of the given copolymers in acetic acid are diluted, the intrinsic viscosity $[\eta]$ increases sharply, exceeding the value for the initial polymer severalfold. An even greater effect of this kind has been observed for the PVA–P-2-VP solution in formic acid, which indicates the occurrence of strong interactions of solvent molecules with the grafted chains, these being responsible for the uncoiling of the grafted chain and the sharp increase in the size of the coils. The weak temperature dependence of the viscosities of the solutions may be an indication of the stability of this conformation. In solvents without an affinity for the grafted branches (for example, in acetone), the values of $[\eta]$ for CDA–P-2-VP solutions initially decrease sharply with increasing content of the grafted P-2-VP and then remain almost unchanged. The different character of the variation of the intrinisic viscosities of solutions of graft copolymers in solvents of different nature can be readily accounted for by the characteristics of the supermolecular structure and the thermodynamic properties of the solutions. For example, the main structural element of the CDA–P-2-VP copolymers obtained from acetone solutions are globules with an indistinct aggregation, in contrast to the CDA network structures. The formation of globules is associated with the coiling up of the grafted branches of the copolymer, because P-2-VP does not dissolve in acetone. The postulated strong binding of solvent molecules by the grafted chains of the copolymer molecule is reflected in the sharp increase in the heats of solution of the CDA–P-2-VP graft copolymers in acetic acid and in the character of the variation of the Flory–Huggins interaction parameters,[55-57] calculated from sorption isotherms.

The poly(vinyl alcohol)–polyvinylpyrrolidinone (PVA–PVP) graft copolymers represent a combination of water-soluble polymers; they are known to be capable of entering into a complex formation reaction as a result of the formation of intermolecular hydrogen bonds between the hydroxy-groups of PVA and the carbonyl group of PVP (this has been confirmed by the large negative free energies of mixing of PVA and PVP [58]). A decrease of $[\eta]$ compared with the initial polymer, the absence of extrema on plots of the temperature dependence of viscosity, and also an increase of $[\eta]$ after the introduction of dimethylformamide (DMF) into the aqueous solution have been demonstrated for aqueous PVA–PVP solutions.[59] The possibility of the occurrence of specific intramolecular interactions in such systems is determined by the ability of the solvent to favour or hinder such interactions.

The differences between the behaviour of two types of macromolecules of graft copolymers based on chlorinated poly(vinyl chloride) (CPVC–PS, CPVC–PVAC†) can be traced from the variation of $[\eta]$ of their solutions in mixed solvents, one of which is selective or is a general precipitant.[56] The extremum in the variation of the viscosity with the composition of the mixed solvent, associated with the microphase separation of the branches of the graft copolymers, which is caused by the incompatibility of the main chain and the grafted chain, is observed only for CPVC–PS.[56] The observed extremum in the variation of $[\eta]$ with the composition of the mixed solvent for the CDA–PVAC, cellulose triacetate–poly(vinyl acetate) (CTA–PVAC), CDA–PVP, and CDA–PAA graft copolymers can be explained by the change in the conformational state of the macromolecules as a result of the rupture of the intramolecular hydrogen bonds.

The different types of behaviour in mixed acetone–methanol solvents of the CDA–PVAC and CDA–PVP graft copolymers are striking.[56] Whereas the variation of the viscosity for the CTA–PVAC system is determined mainly by the characteristics of the interaction of the molecules of the second

† Poly(vinyl acetate).

component of the mixture of solvents with the main copolymer chain, in the CDA–PVP system the influence of the interaction of the grafted branches with the methanol molecules is more pronounced. Furthermore, specific interactions of the type of hydrogen bonding are possible for both components of the CDA–PVP graft copolymers in the binary solvents investigated. The CDA–PAA graft copolymers, whose macromolecules contain hydroxy- and amide groups, also belong to such systems. In the acetic acid–water mixed solvent, the conformational state of the CDA and PAA macromolecule is determined by the different character of their interaction with acetic acid molecules. The behaviour of the graft copolymers in the acetic acid–water system combines a series of effects characteristic of the homopolymers and a distinct dependence of the effects on composition has been observed. Conformational changes in the macromolecules of graft copolymers in mixed solvents have also been observed by Trakhtenberg et al.[60] and Dondos.[61]

The changes in the conformation of graft copolymers can also be traced by means of the anomalous changes in the plot of the viscosities of their solutions against temperature. The extrema in the temperature variation of $[\eta]$ correspond to the conformational transition in which a "segregated" conformation is replaced by a statistical conformation. Such behaviour is common for graft copolymers regardless of the degree of compatibility and the positions of the extrema are almost independent of the composition of the corresponding graft copolymers.[56] Furthermore, such effects are manifested even under the conditions of a strong interaction (of the type of hydrogen bonding). The CDA–PAA–formic acid system, for which the temperature variation of $[\eta]$ is very complex, is therefore of interest.[57] The changes in the conformation of the macromolecule under the influence of temperature in systems of this type can apparently proceed via a series of stages.

## IV. DEPENDENCE OF THE THERMODYNAMIC AND CONFORMATIONAL PROPERTIES OF THE SOLUTIONS ON THE MOLECULAR STRUCTURE OF GRAFT COPOLYMERS

### 1. The Molecular Structure and Conformations of Graft Copolymers in Solution

Major advances have been achieved at the present time in the controllable synthesis of block and graft copolymers. However, few studies of the molecular characteristics and also of the thermodynamic, hydrodynamic, and other physicochemical properties of solutions of graft copolymers have been described in the literature. It is still not clear how the molecular weight, the number of grafted chains, and the degree of compatibility of the components of the graft copolymer, as well as the nature of the solvent influence the conformational parameters and physicochemical properties of such copolymers. By varying the above parameters, it is possible to alter particular properties of the graft copolymers, which enables one to obtain materials with previously specified properties. The influence of the length of the grafted branches on the properties of copolymers in solutions has been investigated.[62–65] It has been established for CDA–PS graft copolymers[62,63] that, firstly, the grafting of PS initially diminishes the $[\eta]$ of the graft copolymer compared with the initial CDA, when the molecular weight of the PS changes only slightly, and, secondly, it leads to an increase of $[\eta]$ of the solutions under conditions of a high content of PS chains, when their molecular weight increases sharply (to $1.08 \times 10^6$), i.e. in this region the influence of the branching and segregation is small and the overall change in $[\eta]$ is determined solely by the length of the grafted branches. Direct determinations of mean square radii of inertia $(\overline{R}_z^2)^{1/2}$ of the CDA–PS solutions in a solvent having the same refractive index as CDA, namely pyridine, have shown that the main contribution to the overall volume of the macromolecule of the graft copolymer comes from the side chain.

Measurements of light scattering by CDA–PS solutions in different solvents have shown[63] that tetrahydrofuran (THF) interacts more effectively with the components of the copolymer. For this reason, the values of $[\eta]$, $(\overline{R}_z^2)^{1/2}$, and virial coefficients $(A_2)$ for solutions of the given copolymers in THF are greater than for DMF. A very sharp increase of $(\overline{R}_z^2)^{1/2}$ is observed in dioxan, where the values of $A_2$ are much smaller than in THF and DMF, which is a consequence of the association of the copolymer macromolecules, indicated by the very high molecular weight $\overline{M}_w$. It is noteworthy that CDA and PS are thermodynamically incompatible[62] and, according to the average free energy of the blending of these polymers, the degree of their incompatibility in THF is much greater than in DMF. Consequently the incompatibility of components of these copolymers promotes a more effective interaction with the solvent.

Another picture is observed for CDA–PVP graft polymers, where the effects of branching and segregation determine the characteristic features of the hydrodynamic properties of their solutions.[64]

The thermodynamic and conformational properties of CTA–PMMA graft copolymers, synthesised by non-terminable radical polymerisation,[66] which makes it possible to regulate the molecular weight and the number of grafted branches, have been investigated. It has been established that, with increase in the number of grafted branches, the values of $(\overline{R}_z^2)^{1/2}$ for comparable molecular weights of the grafted branches and the values of $A_2$ increase. A sharp increase of the molecular weight of the grafted branches entails an increase of the values of $(\overline{R}_z^2)^{1/2}$, while $[\eta]$ changes only slightly. The $[\eta]$ for graft copolymers are very sensitive to changes in the number of grafted branches and increase sharply with increase of the latter. The isotypical character of the variation of $[\eta]$, $(\overline{R}_z^2)^{1/2}$, and $A_2$ for solutions of copolymers with increase of the molecular weight of the grafted branches is noteworthy.

Graft copolymerisation in the presence of cobalt(III) salts, which permits the regulation of the process parameters, has been carried out.[67] The molecular parameters of the graft copolymers of CTA with poly-2-methyl-5-vinylpyridine (PMVP) vary with the polymerisation conditions: $M_{cop}$ from $1.1 \times 10^5$ to $4.45 \times 10^5$, $M_{CTA}$ from $7.5 \times 10^4$ to $3.2 \times 10^5$, and $M_{PMVP}$ from $6.0 \times 10^3$ to $8.0 \times 10^4$. Despite the fact that the average number of units in the main chain between neighbouring branches varies within wide limits, from 45.0 to 712.0, the number of grafted branches increases only to 5.8, which is associated with the fact that oxidative properties, leading to a decrease of $M_{CTA}$, take place simultaneously with graft polymerisation.

The molecular characteristics and the hydrodynamic, thermodynamic, and conformational properties of CTA–PMVP copolymers have been investigated.[67,68] The intrinsic viscosities of the graft copolymers depend significantly on the molecular structure, because the latter determines the degree of branching. It is of interest to compare the dependence of $[\eta]$ on $M_{cop}$ with the analogous data for CTA. The increase of $[\eta]$ for CTA on passing from methylene chloride to formic acid is caused by the change in the conformation of the molecules owing to the specific interaction with the solvent. The intrinsic viscosity $[\eta]$ varies

analogously also for the CTA–PMVP copolymers; [η] for the copolymer is higher in this instance than for CTA with the same molecular weight. Presumably the incompatibility of CTA and PMVP in the solvents indicated leads to an unusual conformation of the copolymer macromolecules, the character of which depends on the quality of the solvent. The difference between the behaviour of the mixture of homopolymers and their graft copolymers can serve as a demonstration, on the one hand, of the grating step which is in many cases responsible for the impairment of the solubility of the graft copolymers with increase of the molecular weight of the grafted branches, and, on the other, can indicate the influence of the nature of the solvent on the thermodynamic properties. The influence of the nature of the solvent is in this case so great that even the signs of the average free energy of blending of polymers are different for the graft copolymers and their blends.[68]

The constants $K$ and $a$ of the Kuhn–Mark–Houwink equation for graft copolymers have been determined.[63,65,69,70] The low value of the power exponent $a$ is striking, indicating a weak thermodynamic interaction of the copolymer and the solvent in the absence of permeability of the copolymer macromolecules to solvent molecules. While the graft copolymers investigated by Klenin and co-workers[69,70] had a comb structure, that of the macromolecules of graft copolymers investigated by Akbarov and co-workers[63,65] must have been of the star type, because the molecular weights of the side branches were very high—much higher than the molecular weight of the main chain. For this reason, the low values of the exponent $a$ for the given copolymers with incompatible components may be a consequence not so much of the branching as of the globular form of the macromolecules, predominantly owing to the long side branches: for long grafted branches, the probability of their selective interaction with one another to form microregions of identical chemical nature increases.

A possible confirmation of the foregoing concerning the dominant influence of long grafted branches on the conformation is the decrease of the values of $A_2$ with increase of the temperature of the solution of the CDA–PS copolymer in DMF, which is confirmed in its turn by data for the phase diagrams and sorption properties quoted by Tashmukhamedov et al.[62] In other words, the CDA–PS solution in DMF has upper and lower consolute temperatures and the region of solubility is extremely limited, while the initial CDA and PS do not separate into different layers either on cooling or on heating. Consequently, even in effective solvents there is a preferential interaction of the chemically homogeneous segments, promoting the formation of microgels and hence the precipitation of the graft copolymer.

## 2. Characteristic Features of the Phase Equilibrium in Solutions of Graft Copolymers

The characteristic features of the structure of graft copolymers consisting of units of chemically heterogeneous components suggest that the critical phenomena in their solutions occur somewhat differently than in homopolymers. Here the main role may be played by segregation or intramolecular phase separation processes caused by the incompatibility of the polymeric components of the graft copolymer. For this reason, the structure and conformational state of the macromolecules of the graft copolymer in solution may have a specific influence on the phase equilibrium, as a consequence of which a difference from the properties of the corresponding initial polymers is ultimately observed.

It follows from the phase diagram obtained[62,71] for CDA–PS solutions in THF, epichlorohydrin, dioxan, and DMF that a characteristic feature of such solutions is the presence in all solvents of a lower consolute temperature of the first type (in Tager's classification) caused by the strong intermolecular bonds between the components in solution, which are broken on heating. It is also evident that, with rare exceptions, an improvement in the solubility of the CDA–PS copolymers is to be expected at room and lower temperatures owing to the influence of the branching of the copolymers.

When the lower consolute temperatures for a solution of CDA in THF and for CDA–PS are compared,[62,71] the observed differences are manifested not only in the consolute temperature and its type but also in the character of the very phase transition in the system. The phase separation in CDA–PS solutions is manifested by the formation of particles of the polymer phase in the form of unusual block formations, leading to, as it were, the "displacement" of the solvent from the solution and to a phase transition in the system. The temperature of the appearance of the first signs of particles of the polymer phase is adopted in this instance as the temperature at which separation into layers occurs. In the case of homopolymers, this is usually preceded by the appearance of a turbidity of the solution (critical opalescence), which has not been observed for graft copolymers. Analysis of the phase diagrams for the system investigated showed that the solubility of CDA–PS is a function not only of temperature but also of the composition of the copolymer,[72] which is common to all the solvents investigated. However, with increased content of PS in the copolymer, a continuous impairment of the solubility is not observed. This interesting feature is demonstrated by the fairly sharp improvement in the solubility of the CDA–PS specimen containing 77.4% PS in all the solvents investigated compared with the copolymers having a lower PS content.[72] Yet another example of such behaviour of graft copolymers in solution is provided by the CTA–PMMA copolymers investigated by Akbarov,[65] thermodynamic properties of which we shall consider in detail below.

It is known that the effect of high pressure on solutions of homopolymers tends to shift the lower consolute temperatures towards higher values and the upper consolute temperatures towards lower values, i.e. it impairs the miscibility in the polymer–solvent system. The literature data for the influence of pressure on the phase equilibrium and the thermodynamic parameters of homopolymer solutions have been analysed.[73] For the phase equilibrium as a function of pressure in block and graft copolymers, there are only a few data in the literature. As an example, one may quote studies on the solutions of CDA–PS graft copolymers in THF.[74] According to the results, the application of a pressure of the order of 20–200 bar tends to improve the solubility of CDA–PS. However, a graft copolymer with a high PS content, characterised by a poorer solubility, requires a higher pressure in order to dissolve, which is a consequence of structural characteristics of the graft copolymers investigated.

## 3. Thermodynamics of the Phase Equilibrium in Solutions of the Graft Copolymers in the Light of the Prigogine–Patterson Theory

The Prigogine–Patterson theory[75,76] is a development of the thermodynamic Prigogine–Flory theory.[77,78] The applicability of the Prigogine–Flory theory, which describes liquid–liquid systems, to polymer solutions has been demonstrated in a number of investigations[79–82] in which reduced thermodynamic functions were calculated for certain polymer

systems. The expression arising from the Prigogine–Flory theory for the interaction parameter $\chi_1$ is

$$\chi_1 = \left(-\frac{U}{RT}\right)\nu^2 + \left(\frac{C_p}{2R}\right)\tau^2 , \quad (1)$$

where $U$ is the configurational energy or the evaporation energy of the solvent, $\nu$ the parameter referring to the cohesion energy and the segmental size of the components, $C_p$ the configurational heat capacity of the solvent, which increases with temperature and tends to infinity as the critical temperature for the transition from the liquid to the vapour is approached, $R$ the gas constant, and $\tau$ a structural parameter characterising the difference between the free volumes of the polymer and the solvent, which can be calculated from the formula $\tau = 1 - T_1^*/T_2^*$, where $T_1^*$ and $T_2^*$ are the characteristic reduced temperature parameters of the solvent and the polymer respectively.

It is exceedingly difficult to use the interaction parameters $\chi_1$ in this expression in order to characterise the mixing of the polymer with the solvent including the region of the [given] phase state. A modified theory put forward by Patterson[75,76] therefore merits attention. He obtained a different expression for the critical interaction parameter having applied the van der Waals principle of the volume dependence of the configurational energy of liquid (this was pointed out previously in an early investigation by Flory[78]) and having expressed all the quantities in Eqn.(1) in terms of the reduced volume of the solvent:

$$\chi_{1,cr} = \frac{c_1\nu^2}{1-\tilde{V}_1^{-1/3}} + \frac{c_1\tau^2}{2\left[(4/3)\tilde{V}_1^{-1}-1\right]} = \frac{1}{2}\left[1+r^{-1/2}\right]^2 , \quad (2)$$

where $\tilde{V}_1$ is the reduced volume of the solvent, $c_1$ the number of degrees of freedom of the solvent molecule, $\nu^2$ and $\tau^2$ are temperature independent parameters or, in terms of Patterson's theory,[76] $c_1\nu^2$ is a factor which depends on the chemical nature of the solvent and the polymer and $c_1\tau^2$ is the structural factor, and $r$ is the number of polymer segments in the micromolecule. As in Eqn.(1), the first term of Eqn.(2) contributes to the variation of $\chi_1$ with decrease of temperature and predicts the upper consolute temperature, whilst the second contributes to the variation of $\chi_1$ with increase of temperature and predicts the lower consolute temperature. According to the theory, $\nu^2 = 0$ for systems having identical or very nearly identical chemical structures and in this case the parameter $\chi_1$ is determined solely by the structural term. Eqn.(2) then has only one root:[76]

$$\tilde{V}_1^{-1/3} = 3/4\,(1 + c_1\tau^2 Q) , \quad (3)$$

where $Q = [1 + r^{-1/2}]^{-2}$. For systems where the polymer and the solvent have different chemical structures, the theory predicts the upper and lower consolute temperatures. Thus, by calculating the molecular parameters in Eqn.(2), it is possible to characterise quantitatively the mixing of the polymer with the solvent as the temperature is varied.

In the Flory equation,[80] the quantity $r$ is determined by the ratio of the molar volumes of the polymer and the solvent, i.e. by $V_2^*/V_1^*$, and $T_1$ is calculated from the equation

$$\tilde{T}_1 = \tilde{V}_1^{-1}\left(1-\tilde{V}_1^{-1/3}\right) = T/T_1^* \quad (4)$$

where $V_1$ is the reduced volume of the solvent, which can be calculated from the formula

$$\tilde{V}_1 = \left[\frac{\alpha_1 T}{3(1+\alpha_1 T)} + 1\right] ,$$

where $T$ is the experimental critical [consolute] temperature, and $\alpha_1$ the coefficient of thermal expansion of the solvent.

The principle of the theoretical analysis of reduced temperatures involves the plotting of two graphs: the first represents the dependence of $\tilde{T}_1$ on $\tilde{V}_1^{-1/3}$ in accordance with Eqn.(4), where $\tilde{T}_1^* = T/T_1^*$ and $T_1^* = T\tilde{V}_1/(1 - \tilde{V}_1^{-1/3})$, while the second represents the dependence of $\chi_{1,cr}$, $c_1\nu^2$, and $c_1\tau^2$ on the same values of $\tilde{V}_1^{-1/3}$, the ranges of variation of the parameters $c_1\nu^2$ and $c_1\tau^2$ being taken from the literature data.[76] The main difficulty consists in the selection of critical values of the parameters $c_1\nu^2$ and $c_1\tau^2$, which must satisfy the theoretical data of Eqn.(2). The points corresponding to the intersection of the horizontal lines for the given values of $\chi_{1,cr}$ and the corresponding suitable values of $\tilde{V}_1^{-1/3}$ yield the temperature variation of $\chi_1$ which is described by Eqn.(2). $\tilde{T}_{1,theor}$ is calculated from the theoretical values of $\tilde{V}_1^{-1/3}$ already obtained in this way. In order to compare the experimental and theoretical $\tilde{T}_1$, the temperature axes are displaced in such a way that these data coincide.

The applicability of the Prigogine–Patterson theory to the description of the phase equilibrium in solutions of polar-rigid-chain polymers of the copolymer type has been demonstrated:[83] CDA in THF and CTA in methylene chloride (MC). Lower and upper consolute temperatures have been observed for the first system and an upper consolute temperature for the second. In the CDA–THF system the shift of the theoretical axis at the upper and consolute temperatures is 12° and 55 °C, while for the CTA–MC system the shift [at the upper consolute temperature] is 1.5 °C. Such a significant difference between the experimental and theoretical data in the region of the lower consolute temperature is a consequence of the fact that the new phase initiation processes, in which the polymer macromolecules are structured and aggregated and there is a transition from homophase to heterophase fluctuations, whose dimensions vary with temperature, are already prepared for in the region remote from the consolute temperature. For systems having both types of consolute temperatures, the temperature dependence of $\chi_1$ has an extremum, which can be below or above the ideal value $\chi_1 = 0.5$. The coordinates of this point are determined from the known limiting value of the parameters $c_1\nu^2$ for the case where an increase in the molecular weight of the polymer entails the mutual approach and possibly even the identity of the upper and lower consolute temperatures, giving rise to the so-called "hour glass" form.[76] This means that, when the molecular weight is greater than a certain critical value, the middle sections of the upper and lower branches of the phase diagrams merge, i.e. there appears a range of compositions where the system cannot exist as a single-phase system at any temperature. In this case the minimum in $\chi_1$ is calculated from the equation

$$\tilde{V}_1^{-1/3} = \frac{7}{8} + \frac{3}{8}(c_1\tau^2 - c_1\nu^2)\,Q , \quad (5)$$

where $Q$ assumes a value close to unity at $M \to \infty$. The limiting values of $c_1\nu^2$ calculated in this way are 0.0255 for CDA–THF and 0.01845 for CDA–MC and are correlated with the plot of $\chi_1$ against $\tilde{V}_1^{-1/3}$ and with its temperature variation.[83]

It is noteworthy that the separation of the interaction parameter $\chi_1$ in accordance with the Patterson theory into molecular parameters is important for the understanding of the temperature variation of the miscibility of the polymer solution. The temperature variation of these parameters obtained by Goloborod'ko et al.[83] from Eqn.(2) is characterised by their different role in $\chi_1$, where the term $c_1\tau^2$, leading to the separation of the system into different layers at high temperatures, makes the dominant contribution. This is apparently a distinctive feature of solutions of cellulose acetates, which are involved in complex intermolecular interaction with the solvent by virtue of the specific features of their structure.

As for homopolymers, when the molecular weight of the graft copolymer increases, the consolute temperatures approach one another, i.e. the usual picture involving an impairment of miscibility with increase of the molecular weight is observed.[74] On the assumption that the CDA–PS specimen with 77.4% PS and a very long grafted chain ($\tilde{M}_\eta$ = $1.086 \times 10^6$) can be regarded by convention and with some approximation as homo-PS, an attempt has been made[74] to apply the Prigogine–Patterson theory to this copolymer.[75,76]

The study of the phase diagrams for solutions of CDA–PS fractions in THF and DMF has shown[74] that this approach to the quantitative description of the phase equilibrium in solutions of graft copolymers is entirely acceptable. The higher theoretical reduced consolute temperatures compared with the experimental temperatures may be regarded as a consequence of the presence of lower consolute temperatures of the first type in solutions of the graft copolymers, whilst the theory provides for the presence of a lower consolute temperature of the second type in polymer systems. Nevertheless the calculated temperature dependence of the parameters of the Patterson equation represents, in the case of CDA–PS solutions, a typical picture of the variation of the phase state of polymer solutions with temperature (Fig.1). The system investigated is characterised by definite values of the structural ($c_1\tau^2$) and chemical ($c_1\nu^2$) parameters, which satisfy the theoretical data of the Patterson equation $\chi_{1,cr} = \frac{1}{2}(1 + r^{-1/2})^2$. For certain values of $\chi_{1,cr}$ and suitable $\tilde{V}_1^{-1/3}$, points representing the temperature variation of $\chi_1$ described by Eqn.(2) are obtained. The value of $\chi_1$ at any point within the temperature range describes the behaviour of the system as a function of the degree of interaction of the polymer with the solvent. According to the results of the calculation of the temperature variation of these parameters, the graft copolymer interacts with the solvents employed to different extents.[74] This conclusion is based not only on data for the consolute temperatures but also on the analysis of the character of the influence of the nature of the solvent on the miscibility with the polymer.

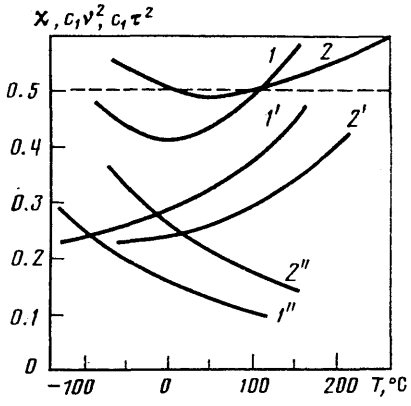



**Figure 1.** Temperature variation of the interaction parameters $\chi_1$ (curves *1* and *2*) and the molecular parameters $c_1\tau^2$ (curves *1'* and *2'*) and $c_1\nu^2$ (curves *1''* and *2''*) of Eqn.(2) for different systems:[74] *1*), *1'*), and *1''*) CDA–PS–THF; *2*), *2'*), and *2''*) CDA–PS–DMF.

## 4. Relation between the Type of Consolute Temperature and the Signs of the Thermodynamic Parameters of Mixing in Solutions of the Graft Copolymers

According to thermodynamic predictions, systems with a lower consolute temperature should be characterised by negative enthalpies and entropies of mixing. On the other hand, for systems which have both an upper and a lower consolute temperature, the enthalpies and entropies of mixing should decrease (i.e. their absolute negative values should increase). The study of the temperature variation of the sorption of dichloroethane vapour by the EPVC–PS graft copolymer[84] has shown that the system becomes unstable with increase of temperature, which is manifested by a decrease in its absolute negative free energy $\Delta g^m$ and indicates the impairment of the quality of the solvent. The data obtained[84] for the temperature variation of the free energy were used to calculate the enthalpies and entropies of mixing. They are negative over the entire temperature and concentration ranges and diminish in absolute magnitude with increase of temperature.

Comparison of the results obtained for the initial polymer and the graft copolymers show that the grafting step impairs the affinity of the solvent for the graft copolymer and limits the region of existence of the homogeneous solution, which is expressed by a decrease in the heat of solution and the free energy and by the appearance of a lower consolute temperature on the mixing diagrams. For CDA graft copolymers, whose grafted branches have different chemical nature, the change in the enthalpy component of the chemical potential makes a significant contribution to the change in the affinity of the solvent for the graft copolymer. Thus CDA–PVAC graft copolymers dissolve in acetone, which is a common solvent for the copolymer components, with a smaller heat change than the initial polymer[85] and the heat of solution falls sharply with increased content of the grafted PVAC in the copolymer.

On the basis of the finding that the interaction of grafted PVAC chains with acetone is almost athermal, one can assume that the observed decrease in the heat changes indicates not only a weakening of the interaction energy of the polar groups of the main chain of the copolymer with the solvent molecules but also a change in the structure of the graft copolymer with increased amount of the grafted polymer. This is also indicated by sorption data,[86] from which it follows that, with increase of the fraction of PVAC chains in the graft copolymer, the sorption capacity diminishes not only for acetone but also for methanol, although in the latter case an increase in the degree of sorption should have been seemingly expected, since methanol is a selective solvent for PVAC. Measurements of the specific volumes have shown[86] that the dissolution of CDA and CDA–PVAC in acetone is accompanied by a decrease in volume, i.e. the criterion of a lower consolute temperature, which obtains for the given system in the high temperature range, holds. The smaller contraction for solutions of the graft copolymer than for CDA is a consequence of the closer packing of the graft copolymer.

It is known that the contraction observed in solutions is frequently the cause of the negative contribution to the heat and entropy of mixing. According to the data obtained,[86] the $\Delta g^m$ for the CDA–acetone system become less negative with increase of temperature, as predicted by thermodynamics for systems having a lower consolute temperature. The thermodynamic functions for PVAC are positive and increase with temperature. It has been found that the behaviour of the graft copolymers is determined by the presence of the grafted component, whereupon the

positive enthalpy and entropy of mixing decrease with increasing temperature. The discrepancy between the type of consolute temperature and the signs of $\Delta H^m$ and $\Delta S^m$ for CDA–PVAC solutions is caused by the sharp difference between the thermodynamic properties of the main and grafted copolymer branches, which is the reason for their incompatibility.

In the study of CDA–PVP and CDA–PAA graft copolymers, it has also been observed[64,87] that the variation of the solubility is determined mainly by the variation of the energy component of the chemical potential. Analysis of experimental data has shown that this situation is common to CDA graft copolymers in the solution of which the energy factor plays a dominant role.

### 5. The Flory–Huggins Theory and Tager's Method in the Study of the Thermodynamic Properties of Multicomponent Systems

The extent of intermolecular interactions in solutions of graft copolymers can be estimated with the aid of the Flory–Huggins theory based on the calculation of the Flory–Huggins parameter $\chi'_{12}$ from Scott's equation.[87] The published determinations of the parameter $\chi'_{12}$ for graft copolymers have been analysed.[7] However, the influence of the length and number of the grafted branches on $\chi'_{12}$ was not investigated in the above studies. Investigations[65,89,90] in which a difference between the behaviour of mixtures of CTA and PMMA polymers and their graft copolymers with different molecular structures was demonstrated are of great interest in this connection (Fig. 2).

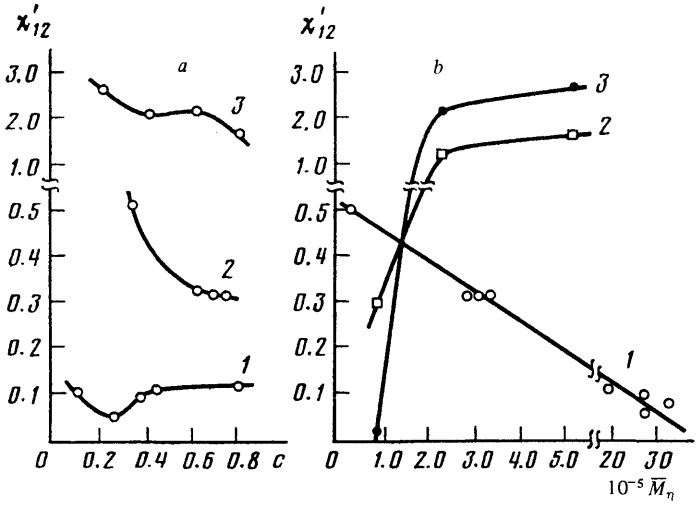



**Figure 2.** Dependence of the polymer–polymer–solvent interaction parameter $\chi'_{12}$ on the content $c$ ($a$) and the molecular weight of PMMA ($b$) in methylene chloride:[65] $a$) CTA–PMMA graft copolymers having grafted branches with high $\bar{M}_\eta$ ($1.95 \times 10^6$–$3.30 \times 10^5$) (curve *1*), CTA–PMA graft copolymers with relatively short grafted branches ($3.30 \times 10^4$ to $3.30 \times 10^5$) (curve *2*), and CTA–PMMA mixtures (curve *3*); ($b$) CTA–PMMA graft copolymers (curve *1*) and mixtures of CTA and PMMA in which the proportions of PMMA are 0.4 (curve *2*) and 0.6 (curve *3*).

The polymer–polymer–solvent interaction parameters $\chi'_{12}$ [or $\psi(a_s\phi_p)$ for graft copolymers], calculated from the Scott, Patterson, and Krause equations using the Flory–Huggins and Flory–Scott theories are directly related to the average free energies of the blending of the polymers $\Delta g_x$ determined by Tager's method.[91] Numerous determinations of the $\Delta g_x$ for polymer blends have been published—by Tager and co-workers[43–45,92,93] for block copolymers, while for the graft copolymers a series of investigations have been made by Tashmukhamedov and coworkers.[62,86,87,90,94] Tager and co-workers[43–45] demonstrated for the first time the possibility of applying Tager's method in the estimation of the thermodynamic stability of blocks in block copolymers and established that the presence of chemical bonds between the blocks of the system investigated impairs their compatibility. However, the influence of molecular weight and of the number of and ratio of the blocks on their compatibility, which would make possible a detailed analysis of the thermodynamic criteria of the compatibility of block copolymers, was not investigated in the above studies.

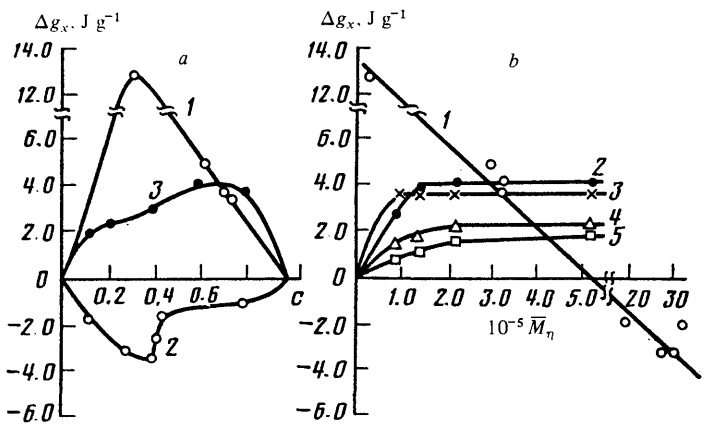



**Figure 3.** Dependence of the average free energy of mixing of the polymers $\Delta g_x$ on the content $c$ ($a$) and the molecular weight of PMMA ($b$) in methylene chloride:[65] $a$) CTA–PMMA graft copolymers having grafted branches with relatively low values of $\bar{M}_\eta$ ($3.30 \times 10^4$–$3.30 \times 10^5$) (curve *1*), CTA–PMMA graft copolymers having grafted branches with high values of $\bar{M}_\eta$ ($1.95 \times 10^6$–$3.30 \times 10^6$) (curve *2*), and CTA–PMMA mixtures (curve *3*); $b$) CTA–PMMA graft copolymers (curve *1*) and mixtures of CTA and PMMA polymers in which the proportions of PMMA are 0.6 (curve *2*), 0.8 (curve *3*), 0.2 (curve *4*), and 0.1 (curve *5*).

Graft copolymers have been studied in detail in a number of investigations[62,63,65,68,95,96] where a study was made of the relation between the molecular structure and the thermodynamic properties of solutions of graft copolymers. It was shown that $\Delta g_x > 0$ for CTA–PMMA graft copolymers with relatively low molecular weights and that the degree of incompatibility is much greater than for polymer blends (Fig. 3). For higher molecular weights of the grafted branches, the $\Delta g_x$ assume low negative values; under these conditions, curve *2*, representing the variation of $\Delta g_x$ with the content of the grafted PMMA branches, shows

a rise, which indicates microlayer formation in the system; this was later confirmed by electron microscope investigations.

The different character of the changes in $\Delta g_x$ with increase in the molecular weight of the second component in polymer blends and in graft copolymers is especially remarkable. Whereas the thermodynamic stability of polymer blends is impaired with increase of the molecular weight of PMMA, for graft copolymers $\Delta g_x$ diminishes to negative values as the molecular weight of the grafted branches rises (Fig. 3*b*, curve *1*). Such behaviour of graft copolymers can be accounted for by the "segregated" conformation of the macromolecules for low molecular weights of grafted branches and by the complete suppression of the segregation effect with increase of the molecular weight of such branches. It is noteworthy that the mean square radii of inertia and the intrinsic viscosities are higher for copolymers with a relatively low molecular weight of the grafted branches compared with those where the molecular weights of such branches are high.[95-97]

## V. THE INFLUENCE OF VARIOUS FACTORS ON THE PROPERTIES OF SOLUTIONS OF GRAFT COPOLYMERS

### 1. The Influence of the Nature of the Solvent

In the case of selective solvents the macromolecules of graft copolymers form monomolecular micelles in dilute solutions; with increase in solvent selectivity or the concentration of such a solution, polymolecular micelles are produced. Strong interactions (of the acid–base type) of the solvent with one of the components of the graft copolymer are fairly distinctly manifested in the character of the structure formation in graft copolymers in solution, in their viscosity properties {there is the sharp increase of $[\eta]$ and its weak temperature dependence} and by an increase of $A_2$ for the solutions.

### 2. The Influence of the Nature of the Polymer

On the basis of the available literature data, one cannot visualise what is the decisive factor governing the compatibility or incompatibility of the polymer pairs and the conformational, thermodynamic, and other physicochemical properties of graft copolymers which follow from this. Polymers having very similar chemical structures may split into separate layers and conversely polymers differing in chemical nature are sometimes compatible.

The nature of the grafted components influences the solubility of the copolymer as a whole, which is due to a change in the absolute chemical potential of the solvent (in some cases a change in the energy component of the chemical potential and in others in the enthalpy component). The change in the solubilities of graft copolymers based on cellulose acetates is determined mainly by the energy component of the chemical potential. The impairment of the dissolving power of the solvent in relation to the graft copolymer is a consequence mainly of the unfavourable changes in the enthalpy component of the thermodynamic potential.

The discrepancy between the type of consolute temperature and the signs of the thermodynamic functions $\Delta H^m$ and $\Delta S^m$ has been observed in certain graft copolymers, which is due to the sharp difference between the properties of the main and grafted chains of the copolymer.

### 3. The Influence of the Compatibility of the Components

In the case of incompatible components, microseparation is observed in good solvents or a preferential interaction may take place between chemically homogeneous segments, favouring the formation of microgels and the precipitation of the graft copolymer.[65]

The conformational properties and structure formation in graft copolymers depends on the compatibility of the components.[65,87] An increase in compatibility entails a decrease of $[\eta]$, $(\overline{R}_z^2)^{1/2}$, and $A_2$ for the solution. In incompatible systems structure formation depends on the nature of the solvent to a greater extent than in compatible systems.[91] The determination of the molecular parameters and the study of the inhomogeneity of the compositions of the CPVC–PS graft copolymer showed that the graft copolymers become inhomogeneous both as regards the chemical composition of the macromolecules and the molecular weight of the components constituting the copolymers.[98]

### 4. The Influence of the Number of Grafted Branches

It has been shown[22] that an increase in the number of grafted branches hinders the formation of polymolecular micelles and that in such cases monomolecular micelles are formed. An increase in the number of grafted branches promotes the formation of a segregated conformation, i.e. microseparation.[65] The intrinsic viscosity $[\eta]$ and $(\overline{R}_z^2)^{1/2}$ diminish for graft copolymers with a small number of grafted branches on microseparation, while in the case of comb copolymers an increase of $[\eta]$ and $(\overline{R}_z^2)^{1/2}$ may be observed.

### 5. The Influence of the Molecular Weight of the Grafted Branches

With increase in the length of the grafted branches, $[\eta]$ and $(\overline{R}_z^2)^{1/2}$ for solutions of the graft copolymers both increase.[62] A marked increase in the molecular weight of the grafted branches can promote the suppression of the segregation effect. It has been shown[65] that graft copolymers with relatively low molecular weights of the grafted branches and a large number of the latter proved to be incompatible and that, when their molecular weight increases considerably, the components become incompatible and the macromolecules assume a more compact form. The second virial coefficient for the solution diminishes with increase in the molecular weight of the grafted branches.[65,95-98] There are no literature data on the influence of the molecular weight of the grafted branches on micelle formation.

### 6. The Influence of Polydispersity and Inhomogeneity of Composition

The graft copolymers employed by Akbarov[65] had grafted branches with a narrow molecular weight distribution. The increments in the refractive indices of the copolymer components proved to be very similar in many solvents, which precluded the determination of the inhomogeneity of their composition and of its influence on the properties of the solutions.

Micelle formation by PVAC–PS graft copolymers in different solvents has been investigated[99] and it has been concluded that the nature of the solvent does not influence the size of the micelles and that the relatively broad distribution of the

micelles with respect to size is a consequence of the polydispersity of the initial copolymers. It has been shown for CPVC and CDA graft copolymers with certain vinyl polymers that, for the copolymers with a marked inhomogeneity of composition and polydispersity, the degree of incompatibility is greater and the values of $A_2$ for the solutions are smaller.[98] The polydispersity of the grafted component leads to a greater incompatibility of the copolymer and the homopolymer in a blend and to an impairment of the solubilisation and the homopolymer by the copolymer.[100]

Thus analysis of studies on the thermodynamic and conformational properties of solutions of graft copolymers has shown that the principal features of the behaviour of the macromolecules of graft copolymers in solution have now been quite adequately characterised on the basis of the quantitative compatibility data. Detailed investigations have been made of the thermodynamics of mixing as a function of the composition and the molecular structure of the graft copolymers. The data obtained have been interpreted in the light of modern views on the nature of polymer solutions taking into account the Flory–Prigogine–Patterson theory. Attention has been concentrated on thermodynamic properties which are most important for the understanding of the interaction of the graft copolymers with solvents of different nature.

At the same time many publications are descriptive in character, because there is so far no rigorous theory of solutions of graft copolymers.

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# Scientific and Technical Progress in the Chemical Branches of the National Economy

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The strategy designed to accelerate the social and economic development of the country put forward at the April (1985) Plenum of the Central Committee of the CPSU has received wide support throughout the nation and has been approved by the XXVIIth Party Congress.

In the political report of the Central Committee of the CPSU to the XXVIIth Congress of the Communist Party of the Soviet Union, M.S.Gorbachev noted that acceleration is in the first place an increase of the rate of economic growth as a result of a comprehensive intensification of production on the basis of scientific and technical progress, a structural reorganisation of the economy, and effective forms of regulating the organisation and stimulation of labour.

In the principal directives for the economic and social development of the USSR in 1986–1990 and in the period up to 2000, it was stated that it was intended to solve the key political and economic problems—to accelerate comprehensively scientific and technical progress, to raise decisively the role of science and engineering in the qualitative transformation of productive forces in switching the economy onto the track leading to comprehensive intensification and in increasing the efficiency of productive forces of the community, and to direct the scientific and technical development towards the solution of social problems.

In the twelfth five-year plan as a whole for the national economy, it is already essential to achieve two-thirds of the growth in the productivity of socially useful labour by employing the advances in science and engineering and by the year 2000 the productivity of socially useful labour must be raised by a factor of 2.3–2.5. The task of the universal husbanding of resources has been set. Thus the increase in the requirements for fuel, energy, raw materials, and other materials should be satisfied to the extent of 75–80% as a result of economies. The energy consumption involved in the national product should be reduced by a factor not less than 1.4 and the consumption of metals by a factor of almost 2.

The XXVIIth congress of the CPSU placed before Soviet scientists the task of vigorously redirecting science towards the needs of the technical re-equipment of the national economy to bring it into closer contact with production and to employ for these purposes new improved forms of integration and interaction, to accelerate the incorporation of the results of research for practical purposes, and to improve the efficiency of academic and branch institutes.

A major role is assigned to chemical science and industry in the solution of the above problems.

One of the effective means of raising the level of the national income, of satisfying the growing needs of the population, and of accelerating scientific and technical progress in virtually all the spheres of activity of Soviet man is increased application of chemistry in the national economy.

After the May (1958) Plenum of the Central Committee of the CPSU, chemical industry developed at a high rate: the output of the principal forms of chemical production increased by a factor of 6–10 and that of individual products by a factor of 50 and more.

It is also noteworthy that the level of application of chemistry to the national economy of the USSR lags behind the corresponding level in the developed capitalist countries

and the majority of countries which are members of the Council for Mutual Economic Aid.

Whereas at the present time the USSR is ahead of the USA in the volume of steel smelted to the extent of 45%, in the production of cement by 60%, and in the production of saw timber by 10%, the output of the chemical industry in the USSR is of the order of 40% of that in the USA and the output of plastics is only 18% and of chemical fibres 30%. The output of the main types of chemical products, especially synthetic resins and plastics, chemical additives, and products of fine organic synthesis lags by a factor of 1.5–2 behind the needs of the national economy.

One should also bear in mind that the assortment of chemical additives, chemical plant protecting agents, paint and varnish materials, reagents and especially pure substances, special purpose rubbers, and products of organic synthesis is also inferior to that available abroad; it is necessary to improve the quality of the cinematographic and photographic materials, magnetic carriers, constructional polymers and general purpose polymers, dyes, chemical fibres, filaments, mineral fertilisers, etc.

Analysis has shown that the chemical conglomerate exceeds at the present time the average industrial indices, per unit industrial output, by a factor of 1.5–1.6 in terms of the capital invested and by a factor of 3 in terms of the energy consumed. The industrial output per worker is approximately 1.5 times higher than the industrial average.

Thus an increase of the technical level of the chemical industry and improvement of chemical technologies has a major influence on the improvement of the most important technical and economic indices as a whole and wide-scale application of chemical products influences the acceleration of scientific and technical progress in the national economy of the country.

In view of this the Central Committee of the CPSU and the Council of Ministers of the USSR approved in October 1985 a combined programme for the application of chemistry to the national economy of the USSR in the period up to the year 2000. The programme provides for the extensive application of new chemical materials and products, for the successful introduction of the Foodstuffs Programme of the USSR, the Energy programme of the USSR, the Combined Programme for the Development of the Manufacture of Consumer Goods and Services, for the improvement of the living conditions of the Soviet people, and for the strengthening of the economy of our country. Also it determines the fundamental indices and directions of scientific and technical progress in chemical industry.

The chemical branches of the economy should ensure an increase of the output of the chemical industry in 1986–1990 by 130–131% compared with 1985 and in the period 1991–2000 by a factor of 1.8–1.9 compared with 1990, should greatly reduce the specific consumption of the raw material and fuel and energy resources, and should greatly reduce the ecological contamination by chemical industry. The contribution of chemical products to the total industrial output, which was 6.3% in 1985, should increase to 8% in 2000.

The successful solution of the problems formulated requires the maximum effort and a high degree of responsibility, conscientiousness, and capacity for organisation from all scientists in branch institutes, academic establishments, and higher educational establishments and all research chemists, designers, technologists, and planners concerned with the creation of new chemical processes, technological devices, and industries.

The solution of the problems placed before the chemical branches of the economy requires a fundamentally new approach to the system used to incorporate the advances of science into industry, a profound reconstruction of the economic mechanism and the creation of an integral, effective, and flexible system of management which would make it possible to realise fully the possibilities of socialism.

The development of new technologies and the creation of a new generation engineering for the reconstruction and technical re-equipment of the existing and newly created industries are essential.

The network of scientific organisations must continuously improve and its organisation and structure must be built up in such a way that problems of the realisation of the research–planning–construction–mass production cycle are solved comprehensively and faster.

Scientific and technical progress in the leading branches of the national economy is impossible without the application of modern polymeric materials. Scientific research into the creation and application of new generation polymeric materials with a set of specific operational properties and into the development of new composite materials resulting from their modification is therefore being continuously expanded.

In the manufacture of polyethylene, it is suggested in the first place that the output of low-pressure polyethylene be developed since this will ensure the expansion of the assortment of different brands of polyethylene and in particular the production of linear high- and low-density polyethylene. This will create a basis for the creation and introduction of new technological processes designed to obtain polyethylene in suspension using new bifunctional catalysts and in solution in the presence of highly reactive catalysts on carriers and there is a prospect of employing ideal displacement reactors with catalysts having a selectivity approaching that of enzyme systems.

The production of high-pressure polyethylene is based on waste-free technological processes in plants with a potential unit output of 75 thousand tonnes per annum, which can be raised to 85 thousand tonnes per annum by increasing the degree of conversion. In many applications high-pressure polyethylene will be displaced by linear high- or low-density polyethylene. It is therefore likely that in the future the development of the production of high-pressure polyethylene will be on a smaller scale and it is suggested that the number of existing industries be redesigned for the production of pseudolinear polyethylene.

Together with polymers produced on a mass multitonne scale, constructional polymeric materials for engineering and technical purposes [polyamides, polyacetals, polycarbonate, polysulphone, poly(butylene terephthalate), etc.], having a set of effective strength and deformation properties in combination with good antifriction and electrically insulating properties and a reduced combustibility, will be developed extensively. These materials are irreplaceable in certain branches of engineering and industry. Their extensive application will make it possible to increase by a factor not less than 2 the productivity of labour, and to reduce by a factor of 10–20 the consumption of metals, and by a factor of 8–10 the consumption of energy.

The modification of existing polymeric materials is a promising and vigorously developing method of preparation of new polymeric materials with properties specified beforehand. Together with the development of traditional physical modification methods by creating compositions comprising mixtures of polymers with fillers, other polymers, reinforced fibres, and laminate materials, the methods of chemical modification in the stages involving the synthesis and processing of polymers have been used on an increasingly large scale. The fundamentally new technology of polymerisation filling is of special interest. In this technology

the active polymerisation centres are fixed in some way on the surface of the filler particles after which polymerisation is carried out directly on such particles, which makes it possible to coat the latter by polymer shells of different shape and composition, achieving thereby the specified microstructure of the composite material.

Vigorous research is being prosecuted on these lines at the present time in many scientific centres of the USSR. The results of some investigations have been applied on an experimental industrial scale and new materials are being widely introduced under real operating conditions.

Polymerisation-filled polyethylene, which has been called komponor, has been manufactured under experimental industrial conditions. This is a constructional material with a high impact strength, constructional strength, frost resistance, low combustibility, and other valuable properties. The resistance of komponor to wear is greater by a factor of 2 than that of world brands of high-molecular-weight polyethylene. Methods whereby komponor can be made into sheets, articles with a specific profile, and other articles, including those for constructional machine engineering, have been developed.

Scientific research designed to create and introduce new types of chemical fibres with a comprehensive set of properties, superior to those of traditional materials, has been extensively developed and is not likely to lose its contemporary usefulness. These include the most promising carbon fibres and the synthetic SVM† cord, high-strength, high-modulus, incombustible, and thermostable fibres, and electrically insulating, chemisorbing, hollow fibres with selective properties. The development of methods of preparation of high-strength and high-modulus fibres on the basis of fundamentally new procedures for the processing of traditional flexible chain polymers is particularly timely.

Specialists in the chemical industry together with scientists at the Lomonosov Moscow State University and the USSR Academy of Sciences have laid the scientific foundations for and deduced a new novel technological principle for the strengthening of fibres made of flexible-chain polymers, which makes it possible to increase by a factor of 1.5 the strength and by a factor of 1.5–2 the modulus of elasticity of synthetic composite film filaments and monofilaments.

Studies in this field are being continued and we can legitimately expect that the introduction of synthetic filaments manufactured by means of the new technology will yield an appreciable economic effect in the future. Thus the strength of cables made of monofilaments is higher by 10–20% than that of cables made of composite filaments having the same linear density. Tests on trawls made of monofilaments manufactured using the new technology demonstrated that their employment will increase the rate of trawling and result in a 10% fuel economy by reducing the hydrodynamic resistance of the trawl.

The new fibres will make it possible in the future to displace completely natural fibres from engineering and to direct the resources thus freed towards the manufacture of consumer goods.

Progress in modern science and the development of atomic and electronic technology and, during the last decade, information transmission technology using fibre optics and biotechnology impose increasingly severe requirements as regards the quality of specially pure substances and chemical and biochemical reagents for technological, analytical, and research purposes.

Much importance is attributed and will be attributed to the development of the manufacture of complexones—a promising class of compounds with a high sorption capacity. The use of complexone in small amounts makes it possible to solve important problems in the national economy with a large economic effect. Thus complexones prevent scale formation in rotation cycles in the water cooling of power generation equipment in electric power stations, in atomic ice-breakers, and in community heating systems. The use of complexones in the extraction of petroleum will make it possible to prevent almost completely salt deposition in the equipment used. Complexones remove interfering metals from liquid fuel, act as flame extinguishers and modifiers of the rate of combustion of solid fuel, and are used successfully in the electronic industry in the etching and thorough cleaning of surfaces. The expansion of the assortment of complexones and an increase of their industrial output are based on continuous waste-free automated technological processes, where the waste from other chemical industries is frequently used as the raw material.

Scientific research into scintillation, optical, acoustic, and semiconducting crystals for quantum electronics has supplied various branches of the national economy with materials whereby the monitoring of the operating conditions of instruments and devices can be simplified.

The latest non-silver materials have led to the prospect of creating optical discs with a higher recording density, a long storage life, and many other advantages compared with traditional magnetic carriers.

Biochemical preparations are already widely used in the food and medical industry, in agriculture, and other branches of the economy. It is noteworthy that the future development of scientific research and the utilisation of its achievements in molecular biology, genetics, biotechnology, and also bio-organic chemistry depends in many respects on the supply of these preparations.

The need to economise water has led to the expansion of the manufacture of polyelectrolytes, ion-exchange resins, organic amines, silicates, and phosphate compounds for the chemical treatment of water for the purpose of its purification and repeated utilisation.

Measures undertaken to economise on fuel and raw materials have led in recent years to an increased requirement for chemical agents such as corrosion inhibitors, biocides, chelates, antioxidants, special purpose surfactants, food additives, and fuel additives.

Scientific developments in the manufacture of mineral fertilisers have been directed primarily to the expansion of the assortment of advanced varieties. The nitrogen conversion processes in the soil are regulated and a more complete utilisation of nitrogen by plants is achieved by introducing nitrogen fertilisers with nitrification inhibitors. The organisation of the manufacture of a new type of liquid nitrogen fertilisers is proposed. They consist of a 32% solution of carbamide and ammonium nitrate and contain almost no free ammonia, which makes it possible to eliminate almost completely the loss of nitrogen.

The production of liquid fertilisers will reduce the cost of their manufacture by eliminating a number of stages in the technological process and also will result in a significant economy of labour concerned with the storage and movement of the material as a consequence of the complete mechanisation of unloading and loading. The possibility of transporting these fertilisers and their storage in the usual containers all the year round in the majority of climatic zones of the country must be included among their advantages.

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†Possibly 'synthetic high modulus' (SHM) cord (Ed.of Translation).

The assortment of phosphorus fertilisers has been expanding due to the production of new highly concentrated fertilisers: ammonium polyphosphate (58% $P_2O_5$ and 12% $N_2$) and calcium polyphosphate (41% $P_2O_5$).

The difficulties in expanding the manufacture of phosphorus fertilisers are due to the inadequate supply of concentrated raw materials. The output of Kola apatite is being stabilised. The entire increase in the amount of phosphorus-containing raw materials will be achieved by employing the ores from the Karatau basin, which are difficult to enrich, and also by including in the economic turnover new deposits located in sparsely populated regions with severe climatic conditions. The ores from these deposits have a low phosphorus content. For this reason, new forms of fertilisers obtained from low-percentage phosphate ores are being developed and tested under industrial conditions. Superphosphate manufactured by means of a new technological scheme involving economies in the consumption of sulphuric acid has been assessed as highly effective. The output of thermophosphates and fused magnesium phosphates will be expanded.

Potassium chloride occupies a leading place in the assortment of potassium fertilisers. The task of expanding the manufacture of chlorine-free potassium fertilisers and in the first place potassium sulphate has now been formulated. The creation and introduction of continuous processes in the manufacture of chlorine-free forms of potassium fertilisers is planned.

From 1988, potassium fertilisers will be produced solely in the granulated and coarsely crystalline form. It will be suitable for use in dry fertiliser mixtures and their losses during transport and the contamination of the environment by dust fractions will be reduced.

Another problem, on which scientists are working, is closely related to the expansion of the assortment of fertilisers—namely the increase of the average content of nutrient substances in mineral fertilisers. Definite advances have already been achieved in this direction. In the XIth Five Year Plan the average content of nutrient substances in fertilisers rose by almost 4% and now amounts to 41.5%. In the immediate future it will be increased to 43–44%. In assessing the importance of this problem, one should bear in mind that an increase of the average content of nutrient substances in fertilisers under the conditions of their present output will reduce the annual amount transported by 5 million tonnes and result in the saving in agriculture of up to 5 million man hours in connection with the employment of fertilisers.

The scientific and technical progress in various branches of the economy is achieved by improving the technology and by employing plants with a high potential unit output. This is clearly seen in relation to the progress in the manufacture of ammonia. The first imported plant had an output capacity of 3000 tonnes of ammonia per year. Plants with a daily productivity of 1300 tonnes are now working in the industry. Altogether about 40 large-scale plants concerned with the manufacture of ammonia are now functioning, which constitutes more than half of such plants in the world.

The application of the technological process for the manufacture of ammonia in plants with a unit output capacity of 500000 tonnes per year makes it possible to reduce by 20 to 25% the energy consumption and by 30% the consumption of natural gas. The economic effect of production in large-scale plants is greater by 20–30% than in traditional plants.

The organisation of the manufacture of sulphuric acid under pressure in plants with a unit output capacity of 700000 tonnes per year will make it possible to reduce, compared with traditional technologies, the unit capital outlay by 20–25% and to increase the labour productivity by a factor of 1.5–2, while the amount of harmful waste discarded into the atmosphere will be reduced by a factor greater than 5. The consumption of metals by the plant will be at the same time lowered by 2200 tonnes.

In the XIIth Five Year Plan, it was proposed to develop a plasma-chemical process for the manufacture of nitric acid directly from air. The new method will make it possible to increase greatly the production of nitrogen fertilisers at a minimum cost.

It is planned to achieve scientific and technical progress in the potassium industry by introducing new devices for the excavation of potassium strata which will increase by a factor of 1.5 the labour productivity and will greatly reduce the amount of waste from potassium undertakings.

A fundamentally new process for the conversion of potassium ores is electrostatic separation whereby a 95% concentrate can be obtained with a significant economy in the energy expenditure (by 20–25%). The new technology enables one to eliminate liquid waste from the manufacturing process and to abolish sludge storage containers. The process is susceptible to automation, which will reduce the amount of labour required.

The structural alteration and expansion of the raw materials base for the manufacture of phosphorus fertilisers will be ensured by enriching poor phosphate ores with the aid of flotation, thermal, chemical, and thermochemical processes. In the relevant branch of the economy much attention is also devoted to the introduction into industry of new methods for the underground and open-cast extraction of phosphate ores, their hydroextraction, and their underground leaching.

Chemical plant protecting agents are important for agriculture. In the relevant fields plans have been laid to expand the range of prepared forms of pesticides to 90–95 items in 1990. Particular attention is devoted to the development and production of preparations used in intensive technologies for the growing of agricultural produce.

The improvement of the structure of pesticides and of their quality will be achieved on the basis of the leading manufacturing processes for preparations with a high selectivity of action, which decompose rapidly in the environment and which make it possible to reduce the norm for their consumption per hectare by a factor of 100 and more compared with those employed at the present time.

One of the difficulties in expanding the assortment of chemical plant protecting agents is the fact that the equipment used to manufacture individual preparations is frequently needed for a single item only and machine constructors are not objectively interested in its production. For this reason, one of the directions to be followed in the development of science and engineering in this field involves the creation of flexible technological systems, the so-called modular plants, which make it possible to manufacture different products using a common raw material or intermediates.

In industrial organic synthesis, new technological processes have been developed and introduced on the basis of modern apparatus systems ensuring the maximum output of the required products and the complex utilisation of the raw material and intermediates.

The plan for the period up to 2000 provides for a radical re-equipment of industry, the development and introduction of highly effective technological plants with a high unit output capacity, the intensification of the existing industries on the basis of new catalysts and catalytic systems, the application of fundamentally new less energy-consuming technologies, and the search for less expensive types of raw material.

In particular, it is intended to create plants for the pyrolysis of petroleum fractions by means of a waste-free technology using heterogeneous catalysts, to continue work on the creation of new types of biodegradable surfactants in order to expand their assortment and applications, to organise the manufacture of n-propyl alcohol and propionic acid in order to obtain chemical plant protecting agents and to employ them as preservatives for grain feed and green forage, to develop and create new industries manufacturing butyraldehydes in the presence of a rhodium catalyst, α-olefins, ethyl methyl ketone, isobutyl methyl ketone, isobutylmethylmethanol, etc., to complete the development of a less energy consuming process for the synthesis of butadiene by the single-stage oxidative dehydrogenation of butane in fluidised bed reactors, and the single-stage synthesis of isoprene from isobutene and formaldehyde with a unit output capacity of 120000 tonnes per year, which is characterised by an amount of waste water smaller by a factor of 6, energy requirements smaller by a factor of 2.6, and the consumption of formaldehyde per tonne of isoprene smaller by 25%.

The introduction of the above and other processes will permit the maximum satisfaction of the needs of the national economy for the products of organic synthesis, to reduce the consumption of raw materials and energy resources, and to achieve a saving amounting to more than 250 million roubles per year.

The problem of supplying the tyre and rubber industries with general purpose raw rubbers has now been virtually solved and the proportion of the required imported natural rubber is minimal. For this reason, in the XIIth and subsequent Five Year Plans, development of special purpose raw rubbers has been emphasised, namely the development of modified raw rubbers and both low-molecular-weight and other thermoelastoplastics, which sharply improve the quality of rubber mixtures and reduce the labour involved in their processing.

It is planned to organise the large-scale manufacture of ethylene-propene rubbers at the Nizhnekamskneftekhim PO and acrylate rubbers for the manufacture of technical rubber articles with high heat and oil resistances, to introduce thermoelastoplastics which it will be possible to process by casting under pressure and by extrusion, to eliminate the vulcanisation stage which will permit an appreciable increase in labour productivity, to improve the quality of the product, to reduce the norm for the consumption of the raw material and other materials, and to reduce the amount of imported materials. It is intended to introduce butadiene-styrene rubbers manufactured by solution polymerisation (DSSK). Their application in the tyre industry will increase the useful life of tyres by 5%, while in the light industry their use will increase the wear and frost resistance of shoe sole rubbers and in the manufacture of technical rubber articles it will lead to an increase of the heat resistance and useful life of conveyor belts by a factor of 2–2.5.

The tyre industry has at the present time an output capacity of 74 million tyres. For this reason the main task is to increase the quality of the tyres by increasing the output of radial metal-cord tyres and by employing new types of chemical additives which sharply improve the quality of rubber. The increase in the volume of production of radial tyres will be achieved by the reconstruction and expansion of the existing undertakings and by eliminating cross-ply tyres from industrial production.

At the same time it is planned to develop and introduce advanced equipment for the assembly and vulcanisation of tyres. Thus it is intended to improve the manufacture of light tyres by creating preparation-assembly aggregates of automated machines using manipulators. A technology and equipment have been devised for the vulcanisation of tyres using ultrahigh frequency currents.

The output and assortment of retreadable tyres have increased, including an increase in the output of retreaded radial tyres.

In the industry concerned with technical rubber articles provision is being made for the introduction of processes for the preparation of articles and materials from liquid hydrocarbon rubbers, which will increase the labour productivity by a factor of 2–3 and improve the quality of the articles. Work will be continued on the creation of technical rubber articles from powdered rubber mixtures. The application of this technology will reduce by 30% the consumption of the rubber mixture, by a factor of 1.5 the labour expended at the moulding and vulcanisation stage, and by a factor of 2 the amount of waste.

In the manufacture of flat wedge-shaped and ventilated belts, an improvement in quality together with an increase of useful life by a factor of 1.8–2 by improving the construction and technology of their manufacture and by using new materials are planned. Thus provision is made for the organisation of the manufacture of flat belts with polyamide cores and driving belts with a low transmission capacity from thermoelastoplastics.

The June (1985) conference at the Central Committee of the CPSU on the questions of acceleration of scientific and technical progress was devoted to a profound analysis of the existing situation as regards problems involved in the introduction of scientific developments into industry and the search for reserves which could alter radically the existing situation and increase the technical level of the industries and the quality of the products.

Problems concerning the improvement of the network of scientific organisations and an increase of their effectiveness were carefully examined at all levels of management of different branches of industry.

Comprehensive study led to the proposal for a series of organisational and technical measures and proposals have been developed for a radical improvement of the planning system and the stimulation of work on the creation of a new technology.

The most effective form of the association between science and industry under modern conditions is the Scientific-Industrial Association SIA (NPO in Russian).

In his report at the XXVIIth Congress of the CPSU "The Fundamental Directions of the Economic and Social Development of the USSR in 1986–1990 and in the Period up to 2000", N.I.Ryzhkov said: "It is necessary to work faster on the organisation of scientific-industrial associations. They have been called upon to be at the cutting edge of scientific and industrial progress. Solely by carrying out simultaneously different stages of the necessary work, by liquidating superfluous units, and by centralising management, the duration of the development cycle from research to incorporation into industry has been reduced in leading SIA on average by a factor of 1.3–1.6. The SIA have the necessary component elements for the application of their achievements in industry: scientific establishments, an experimental base, a planning section, and initiating and adjustment subsections—they act directly in the undertaking having been given by it the task of organising the future industrial plant; at the end of its construction they hand over to the undertaking the plant as a growing concern".

This form of organisation enhances the aspect of planning concerned with its programme and aim and shortens the time taken to execute the programmes.

In 1986–1987 the work on the creation of new SIA will be continued and after its completion more than 70% of the expenditure on science and on the employment of scientific workers will be concentrated in them.

In order to solve the strategic problem of accelerating the social and economic development of the country formulated by the April (1985) Plenum of the Central Committee of the CPSU and the conference of the Central Committee of the CPSU on the problems of the acceleration of scientific and technical progress, the concentration of forces and means on the priority fields of science and engineering in order to gain world leadership in such fields in the shortest possible time has acquired the greatest importance.

The decision of the Central Committee of the CPSU and the Council of Ministers of the USSR to create interbranch scientific-technical complexes and to undertake measures to ensure their proper activity has been approved. It is proposed to create in the principal fields of scientific and technical progress interbranch scientific-technical complexes designed to perform the entire cycle of work on the creation and introduction into industry of highly effective types of engineering, technology, and new generation materials and at the same time to reduce severalfold the duration of the work cycle from scientific research to practical introduction of its results into the national economy.

Scientific research establishments, constructional and technological organisations, and the associations and undertakings of the Ministries and Departments of the USSR and the Union Republics which possess the required scientific and technical potential in the relevant fields and which assist in the comprehensive solution of problems are involved in the work of the interbranch scientific-technical complexes.

The interbranch scientific-technical complexes are the leading organisations in the country concerned with the performance of tasks, given to them, in the field of science and engineering and the financial, labour, and material-technical resources, specified capital investments, and contract work, which are necessary for the realisation of plans, will be provided for in the first instance in the plans of the Ministries and Departments within the system of which these complexes are included.

Two interbranch scientific-technical complexes ISTC (MNTK in Russian) have been created for the priority fields of the chemical branches of the national economy: the "Catalyst" ISTC, the "Membranes" ISTC, and, in the field of biotechnology, the "Biogen" ISTC have been set up.

Catalytic processes, which significantly expand the possibilities and radically alter the structure of the consumption of raw materials and intermediate products, have acquired special importance in our time. Nowadays 80–85% of technological processes in the chemical industry are performed with the aid of catalysts and the total output obtained in catalytic processes has been estimated as approximately 1/5 of the entire world industrial output.

The development of catalysts is a key problem in the realisation of the fundamental pathways leading to technical progress in chemical industry, ensuring a transition from extensive to intensive forms of industrial production. The creation and utilisation of more active catalysts leads as a rule to the possibility of increasing the productivity of plants as a whole without their reconstruction. Thus, catalysts so active that they can yield up to 1.5–2 tonnes of the polymer per gram of the catalyst have been created for polymerisation processes leading to polyethylene. Such a small amount of catalyst can be left in the bulk of the polymer without impairing its quality and hence one can exclude from the technological scheme the washing stages which consume up to 40% of the entire capital expenditure on the industrial process. The application of highly active catalysts will make it possible to improve the technological parameters of many processes. For example, it will be possible to reduce the pressure from 200 to 30–50 atm in the manufacture of high-pressure polyethylene and from 300 to 100 atm in the manufacture of methanol. The period in which industrial catalysts are renewed is 7–10 years at the present time and it is planned to renew the most important catalysts each 4–5 years in the future.

Apart from the radical improvements to industrial technological processes, the development of the science of catalysis makes it possible to predict the creation in the immediate future and even more so after 10–15 years of tens of fundamentally new catalytic processes which will significantly expand the possibilities of chemistry and alter radically the structure of the consumption of raw materials and intermediate products. For example, the processes involving the formation of motor fuels and many chemical intermediate products from a mixture of carbon monoxide and hydrogen obtained by the conversion of natural gas and the gasification of coal are very close to practical realisation. This will mean a transition in the future from expensive petroleum to a new raw material in a major branch of the chemical industry, which will involve the manufacture of high-octane petrol, aromatic hydrocarbons, and polyolefins. Methanol is an important chemical raw material. Acetic acid is already being synthesised from it and a process involving the synthesis of formic acid, an important feed preservative, is undergoing experimental tests. One may expect the creation of new processes leading to the synthesis of acetaldehyde, ethylene glycol, ethanol, glycerol, carboxylic acid esters, and many other important chemical products. Processes involving the catalytic stereospecific synthesis of optically active aminoacids—feed additives and pharmaceutical preparations—and also bio-organic processes carried out with the aid of immobilised enzymes, for example, the preparation of sugars from waste in the processing of wood, etc., are close to being realised. Catalysts accelerating the conversion of coal into a synthetic liquid fuel, which constitutes an important contribution to the solution of the fuel and energy problems, are being created. For each chemical process, the trend towards a rational utilisation of energy is extremely specific. Thus, whereas the activation energies for thermal processes are 120–160 and sometimes up to 200 kJ $mol^{-1}$, in catalytic processes the energy falls to 20–30 and sometimes to 7–8 kJ $mole^{-1}$, while in processes involving bio-organic enzyme catalysts it falls even to 1 kJ $mol^{-1}$ and below. Thus the development of an active catalytic system for the synthesis of aliphatic amines made it possible to achieve a saving in the energy resources by 15%, while the intensification of the synthesis of polyethylenepolyamines in the presence of new catalytic systems resulted in a 60% saving.

The possibilities inherent in the introduction of membranes and the membrane technology into different branches of the national economy are very great. For example, the introduction of the membrane technology into thermal power engineering reduces the amount of waste water in the thermal power plant by a factor of 4 and reduces the consumption of alkali and acid by 50%.

The introduction of the resources-conserving membrane technology into the food industry may also serve as an important component for the successful realisation of the Food Programme. The membrane purification, clarification, and stabilisation methods in the production of sugar, juices, and alcohol-free drinks and also in the extraction of food dyes, plant proteins, and other useful substances from the waste generated in the processing of food products make it

possible to reduce greatly the energy expenditure in the preparation of food products, to improve their quality, to increase the storage time and food value of the products by means of cold sterilisation, to extract additional amounts of food raw materials which were hitherto irretrievably lost, and to reduce the contamination of the environment by the waste from food industries. The application of membrane processes in the combined processing of milk and secondary milk products will greatly reduce the energy consumption in the relevant industries, will increase the output of the finished products, will increase the assortment and quality of such products, and will greatly reduce the cost of transport in the delivery of the milk raw material. The introduction of methods for the storage of fruit, vegetables, and grain in a modified gaseous medium using membranes increases the storage time and makes it possible to supply consumers with fresh produce all the year round with a significant reduction of losses during the storage process.

The role of membranes and membrane technology in the protection of the environment from contamination is incontrovertible. Membrane devices and apparatus are used for the analytical monitoring of the environment (sewage and gaseous waste). Furthermore, the use of membrane technology leads to the possibility of creating effective desalination processes for salt and brackish waters and also the creation of closed water cycles in industrial manufacturing processes.

One of the most important ways of increasing the technical level of the chemical sub-branches in industry and of carrying out the tasks involving their intensive development consists in the comprehensive expansion of the cooperation with the Academy of Sciences of the USSR, the Academicians of the Academy of Sciences of the Union Republics, and higher educational establishments in the USSR.

It is generally known that, whatever the advances in the relevant fields of science, it is impossible to raise the technical and economic level in industry to leading positions without an adequate and profound fundamental effort and without cooperation with academic organisations and higher educational establishments. For this reason, starting from the Tenth Five Year Plan, nine regional centres, covering the entire Soviet Union and coordinating joint research and developments, have been active in chemical industry. This is consistent with the task formulated in the report by M.S.Gorbachev at the June conference in the Central Committee of the CPSU, who noted that: "... we should look upon scientific tasks through the prism of the requirements of the present time—requirements for the decisive redirection of science towards the needs of the consumer industry and of the industry towards science. All the units of the chain connecting science, engineering, and industry must be analysed and strengthened from these standpoints".

During the Eleventh Five Year Plan 80 higher education establishments and 95 academic institutes participated in the joint developments concerned with the coordination of plans with branch institutes. The effectiveness of such cooperation is evident. Thus the theoretical principles and technology of the industrial manufacture of film filaments for hay binding twine were developed and the production was organised jointly with the Lomonosov Moscow State University. This made it possible to satisfy fully the needs of agriculture and to achieve a saving amounting to 73 million roubles. A theoretical and practical approach to the welding of polymeric materials, especially polymer tubes, was developed for the first time in world practice jointly with the Paton Institute of Electric Welding of the Ukrainian Academy of Sciences. This problem has now been solved. The economy now receives plants for the welding of polyethylene tubes having diameters ranging from 11 to 1200 mm.

Many such examples can be quoted.

At the same time the existing level of cooperation does not satisfy all the increasing modern needs by academic institutes and higher education establishments. The absence of an adequate experimental base retards the application of the results of completed research in industry. Also the problem of the economic stimulation of the participation of scientists at academic institutes and higher education establishments in the incorporation of scientific developments in industry has not been solved.

In laying the plans for the XIIth Five Year Plan, a fundamentally important resolution was adopted, namely the resolution to achieve a transition to improved forms of planning of joint developments—a programme for the interdepartmental scientific and technical cooperation of the Ministry of Chemical Industry, the Academy of Sciences of the USSR, the Academies of Sciences of the Union Republics and the higher education establishments controlled by ministries.

The principal methods of cooperation for 1986–1990 and for the period up to the year 2000 have been approved. The most important of these is the creation of a new generation of technological processes based on the fundamental work already completed. A comprehensive Programme for scientific and technical progress in the member countries of the Council for Mutual Economic Aid CMEA (Russian abbreviation SEV) up to the year 2000 was adopted at the 41st session of the CMEA. The meeting of the General Secretary of the Central Committee of the CPSU Comrade M.S.Gorbachev with the heads of delegations of the socialist countries and the Secretaries of the Central Committees of the fraternal parties, participating in the session of the CMEA, was especially important. The fundamental approach to the radical questions of the acceleration of scientific and technical progress and internal economic and international politics described at the meeting received full support and understanding.

The consistent realisation of the Comprehensive Programme will accelerate the social and economic development of our country and fraternal states on the basis of the latest scientific and technical advances, will ensure a radical improvement in labour productivity, and will strengthen technical and economic independence. A more complete utilisation of the possibilities of the economic interaction with fraternal socialist countries in ways including the application of progressive forms—wide-scale scientific and technical and industrial cooperation, direct links, and the creation of joint associations and undertakings—is linked to the Programme's realisation.

Major tasks within the framework of the Comprehensive Programme are also to be performed by chemists. Thus in the field of "Biotechnology" the USSR, Czechoslovakia, Hungary, and the German Democratic Republic will create a joint assortment of hundreds of named reagents which will improve the scientific level and shorten the time taken for research in the field of genetic engineering, biology, and biochemistry. New generations of medicinal and enzyme preparations will be introduced into the health service.

New biological plant-protecting agents and veterinary preparations will be introduced for the needs of plant cultivation and animal husbandry.

An important role is attributed to an increase of output in the manufacture of protein feeds.

In the field "Electronisation of the National Economy", technologies have been developed for the manufacture of tens of designated new specially pure substances for microelectronics, including the equipment for their industrial manufacture, analytical monitoring methods, and special

packing. This will improve the speed and reliability of the operation of electronic circuits in electronic computers and will increase the sensitivity of various instruments.

Technological plants based on the block-modular principle will be developed and created jointly with Czechoslovakia, which will permit the manufacture of a large assortment of low-tonnage chemical products with the aid of rapidly readjustable schemes.

Tasks directed to the creation of new polymeric materials for radioelectronics, electrical engineering, machine construction and other leading fields are planned within the framework of the priority field "New Materials and the Technology of Their Manufacture and Treatment". The application of these materials in place of traditional ones will ensure technical progress in the branches of economy consuming them and will increase the reliability and useful life of the products in the course of their employment and will reduce their cost.

Provision is also made for the development and introduction of new and improved technological processes for the manufacture of polymeric materials and articles made from them with a wide-scale employment of computer and micro-processor technology and highly selective catalytic systems stimulating energetic effects.

The task of accelerating scientific and technical progress imposes new, more stringent, requirements on cadres and the style and method of their work. There is a need to achieve throughout a freedom from conservatism, paper work, and a formal attitude to work. The complex and large-scale tasks formulated by the Party require a creative initiative and diligent labour by each worker in chemical industry. The successful performance of the planned tasks and the making of scientific and technical progress in the major fields of development of the given branch of the national economy are the tasks faced nowadays by workers in Soviet industry.

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# Problems in Modern Chemistry

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This review deals with the fundamental problems and the main directions of modern chemistry whose current developments offer both immediate and prospective practical advantages while stimulating continuing progress in chemistry and in related areas of science and technology.

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## I. INTRODUCTION

In sciences (as in any other creative activity) the creative process is less important than its outcome, and seeking is less important than finding. However, finding without seeking is an exceedingly rare occurrence, and therefore most of the effort, expenditure, and resources in science are devoted to seeking. Modern science is an expensive undertaking, and society cannot allow its scientists to engage in aimless searches. Of course, one can stumble on something interesting and valuable even on the path of aimless research, but no serious research worker will wish his success to be determined by the laws of chance. Every investigation, every scientific endeavour should have a declared aim, and should be able to predict the practical results and potential applications of the work and to evaluate its contribution to related fields of science.

Modern chemistry is a many-sided undertaking, involving extensive enquiries in many different directions. Many of its branches have developed into sciences in their own right (inorganic chemistry, colloid chemistry, radiochemistry, organic chemistry, analytical chemistry, physical chemistry, crystal chemistry, chemical physics, electrochemistry, geochemistry, biochemistry, polymer chemistry, etc.). Each of these sciences has its own objectives and well defined boundaries, its own problems, its experts, and its acknowledged leaders. However, in modern chemistry we find many fundamental problems which are common to a variety of areas of enquiry: these attract the combined attention of all branches of chemistry and stimulate contributions from all chemical sciences, whatever their specific objectives and problems. It is important to recognise these "cosmopolitan" problems so as to formulate clearly the most important directions in which further advances can be expected and to achieve greater coherence, relevance, and therefore also effectiveness of the work.

The aim of this review is to define the most important problems in modern chemistry, to present a predictive analysis of their recent developments, and to identify the most timely and relevant achievements.

## II. CHEMICAL STRUCTURE AND FUNCTION

The number of known chemical compounds (approximately eight million at present) is still growing rapidly. The atomic-molecular architecture and electronic structure of these compounds (whether extracted from naturally occurring materials or synthesised) vary between wide limits. Their physical and chemical properties, and therefore also their functions, show similarly extensive variations. In order to identify a substance having prescribed properties and applications (i.e. a prescribed function) we usually need to examine between 3 and 10 thousand compounds: the ambitious task of converting a prepared compound into a substance aimed specifically at serving mankind and at advancing civilisation has a disappointingly low effectiveness. Clearly, establishing a relation between the electronic structure of a compound or material and its functional behaviour is a problem of fundamental importance, which must be solved if we wish to predict the function and usefulness of a substance. In practice the inverse problem is even more important: how should a substance be constructed, what should be its molecular architecture and electronic structure, in order to achieve a prescribed set of properties and a required function?

Modern chemistry has had some undeniable (though modest) successes, based on a rich and varied stock of experimental results, in the solution of both the direct and the inverse problem. We can now confidently predict the dependence of the polymerisation behaviour of monomers on their structure, the main types of chemical reaction and the reactivity of various functional groups, the changes in the electrophysical properties of semiconductors caused by changes in their structure, etc.

A clear example of a successful search for the relationship between structure and function is provided by the synthesis of organic and metal-organic electrical conductors: molecular metals (see Chapter V). Thus the compound $Hg_{3-\delta}AsF_6$, synthesised in 1971, has a high, typically metallic conductivity, and becomes a superconductor at low temperatures. Chemical analysis gives this compound the composition $Hg_3AsF_6$, but

the geometric dissimilarity between the position of the constituent atoms in the crystal lattice produces vacancies of $AsF_6$ groups, so that the composition of the unit cell becomes $Hg_{3-\delta}AsF_6$, where $\delta = 0.18$. The unit cell of a crystal of this compound (Fig.1) shows an unusual molecular structure, consisting of two components: a framework of $AsF_6^-$ anionic octahedra and cationic chains of mercury atoms, accommodated within the channels of the anionic framework along the principal axes (*a* and *b*) of the crystal.

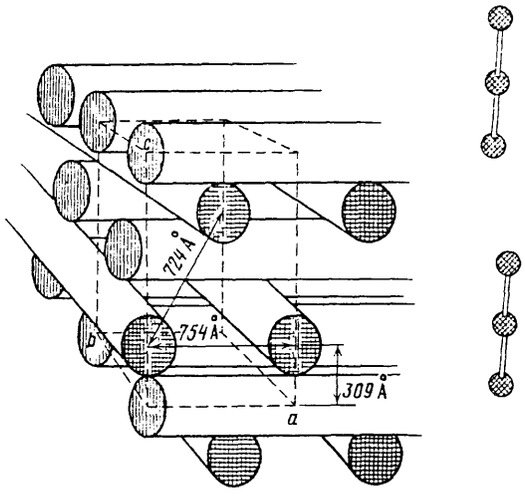



Figure 1. Molecular-structural organisation of $Hg_{3-\delta}AsF_6$; the cationic chains of atoms are shown as cylinders, between which are located the anionic $AsF_6$ octahedra.

This structure imparts special electrical conduction features to the material. The chains of mercury atoms behave as a one-dimensional ordered metal with a high conductivity. This feature results in an electrical conductivity in the crystal along the chains (i.e. in the *a* and *b* directions), coupled with a low conductivity in the perpendicular direction (i.e. along the *c* axis). Lowering the temperature activates the interaction between the conducting chains (first the parallel, and then the perpendicular), leading to superconductivity at temperatures below 4.1 K.

The most important feature of this crystal structure are the linear chains of atoms with delocalised (generalised) electrons, which are responsible for the new function of the material: its metallic conduction and superconductivity. The concept of this structural feature is exploited in all attempts to synthesise molecular metals: organic substances in which $\pi$-electron molecules are packed in the crystal as one-dimensional chains with overlapping delocalised $\pi$ electrons. The motion of the electrons along the chains is responsible for electrical conduction in these compounds, and occasionally for superconductivity at low temperatures (see Chapter V). The structure of one typical organic superconductor, [*bis*(ethylenedithiolo) tetrathiofulvalene]$_2^+I_3^-$, is shown in Fig.2.

Establishing the correlations in the structure–property–function chain is the scientific aim of chemical materials science, and is directly relevant to the development of any new material (polymers, phosphors, materials for semiconductor and laser technology, chemical reagents and catalysts etc.) It is especially important in biochemistry and medicine, where the functional properties of medicinal preparations, hormones, and other physiologically active compounds determine their functional effects in living organisms. This is a very large field, which includes major topics such as the chemistry of memory and the chemistry of thought (a relatively obscure subject, with fundamental practical and intellectual connotations).

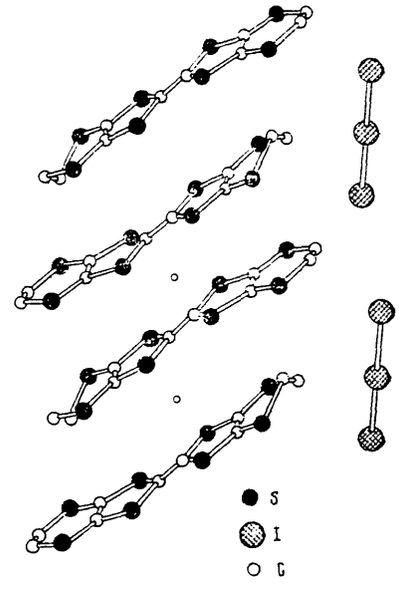



**Figure 2.** Projection of the crystal structure of the organic superconductor [*bis*(ethylenedithiolo)tetrathiofulvalene]$_2^+I_3^-$.

We can solve the direct problem, i.e. establish the structure–function relationship, at two distinct levels: the empirical level, confined to a simple formulation of the relationship between structure and function, and the non-empirical level, involving the study and the identification of the atomic-molecular mechanism by which a given structure can fulfil its function. However, modern chemistry can often formulate and solve the inverse problem: to create a structure having a prescribed function. For example, substances having oxidising properties stronger than those of normal oxidisers ($F_2$, $PtF_6$, $RhF_6$, $IF_5$, etc.) are needed in chemical synthesis. Compounds of the "inert" elements (xenon and krypton) were obtained by using the new oxidisers. The strongest oxidisers ($ICl_5$, $AuF_6$) should activate other elements of Group VIII, and induce previously unreported chemical reactions. This hope is not unrealistic: not many years ago the preparation of chemical compounds of xenon would have seemed out of the question, and yet these compounds are now a conventional part of the chemist's working arsenal. Stable organic paramagnetic materials are now equally familiar: the nitroxyl radicals, which offer a range of functions and are therefore

widely used in physics, chemistry, molecular biology, medicine, and technology.

A similar problem can be formulated in respect of high-energy substances, involving the search for chemical structures with a high energy content. One path to this goal is the synthesis of compounds with atoms in unusual valency states or with an unusual hybridisation of chemical bonds (for example, organic compounds containing a non-tetrahedral saturated carbon atom). This type of problem can (and should) be formulated in all branches of chemistry.

Quantum theory has a large part to play in solving these problems, and its status and role in modern chemistry are beginning to change very markedly. Whereas the task of quantum chemistry was previously to seek (often, successfully) an explanation of the physical origin of various chemical phenomena and structural-chemical effects, its principal aim is now the theoretical prediction of chemical structures, of their existence regions and stability conditions, and of whether their synthesis can be realistically attempted. In this sense quantum chemistry has now moved into the front rank of chemical science, where it directs the experimenters towards molecules and substances with realistic thermodynamic and energy parameters. This new style of quantum chemistry is already apparent from the effort now devoted by quantum chemists to calculations of "exotic" molecules (for example, molecules with a non-tetrahedral carbon atom, hypermetallic molecules, hypothetical "spherical" molecules containing 120 or 60 carbon atoms in $sp^2$ hybridisation, with a high electron density inside the sphere. The molecule with 60 atoms has been called footballene because of its outward similarity to the ball used in that game).

Both the chemical structures and the functions of substances are extremely varied, and the relationships between them are even more varied; the development of adequate systematics is therefore an urgent problem at present. Existing classifications distinguish types of substances by structure-chemical criteria (aldehydes, sulphides, ketones, fluorides, olefins, chalcogenides, etc.) rather than by functions. Modern chemistry requires, in addition, a systematisation based on the structure–property–function principle. Computer-accessible chemical data-bases should play an important part in its development (banks of structural-chemical and functional data, computer systems for identifying and distinguishing chemical compounds according to their functions, etc.). The development of these new methods of classification and the establishment of relationships in structure–property–function series should offer an effective and clear strategy of scientific enquiry in the field of chemistry.

## III. CONTROL OF CHEMICAL PROCESSES

The complexity of chemical processes can be both troublesome and advantageous to the chemist: it allows the adoption of a flexible hierarchy of methods of process control at various levels, from the atomic–molecular level to the level of supermolecular organisation and organisation in terms of mass and energy transfer, aimed at establishing a state of concentration and energy "comfort" for the chemical process.

A chemical reaction is a physical process resulting in the regrouping of atoms and the rearrangement of electronic shells, leading to the conversion of the initial species (reagents) into the final products. The process is controlled by two fundamental characteristics: energy and angular momentum (the moment of the quantity of motion). The importance of the former has long been recognised in chemical science, whereas the role of angular momentum in chemical reactions was recognised only recently.

The great majority of chemical reactions require additional energy to be supplied to the reacting species in order to overcome an energy barrier. The height of this barrier (or, in other words, the amount of energy to be supplied to a particle to allow it to react) is a problem for which a general solution has not yet been found. Theoretical calculations of barriers and of potential energy surfaces for chemical reactions by the most recent techniques of quantum chemistry (non-empirical or semi-empirical) have failed to solve the problem so far: they are cumbersome, their scope is limited, and they are often unreliable. Many empirical relationships for calculating energy barriers and reaction rates (Polanyi's rule, Hammett's equation, Tafel's law, the Woodward–Hoffman rules, the Brønsted–Winstein relation, etc.) are also of limited application as well as being only rough approximations. On the whole, the problem of chemical reactivity—i.e. of the relationship between the electronic and nuclear structure of chemical species and the rate (or barrier height) of their reactions is a classical on-going problem, still far from being solved. This is mainly because the range of chemical species (atoms, molecules, ions, radicals) is enormous, offering a wide range of Coulombic or exchange interaction potentials and of chemical reaction paths. The multitude of types of electron shell and of paths available for their transformation prevents the development of a single, general quantitative theory of chemical reactivity, though in terms of theoretical physics the most elementary chemical interactions are relatively simple and consist exclusively of electromagnetic interactions (nucleus–nucleus, electron–electron, and electron–nucleus).

Controlling a chemical reaction, i.e. changing its rate or its direction, implies firstly changing the height of the energy barrier and secondly adding energy to the internal degrees of freedom in a form usable by the chemical species in overcoming the barrier.

The first control principle is chemical: it relies on modifying the electron shells of the reacting particles by solvation or complex formation. The study of solvation with the aim of discovering effective means of controlling the reactivity and the direction of chemical reactions is one of the main topics of modern chemistry. The main contribution to solvation effects usually comes from complex formation. Modern physical methods have led to important advances in our understanding of complex formation: direct evidence of the delocalisation of the electron shells of the partners in the complex has been obtained, the electronic orbitals involved in the "joint" between the partners have been identified (in some cases), the main types of complex have been recognised and the diagnostics and criteria of complex formation have been formulated, the structural, physical, and dynamic properties of many complexes have been determined, and it has been established that even in the gas phase, chemical reaction is often preceded by complex formation.

Complex formation should affect the reactivity of any chemical species, since it influences the distribution of electric charges, the energy of the molecular orbitals, and the geometric screening (and therefore also the energy barrier) which the reaction must overcome. A much more difficult problem is to establish the extent and the direction of the resulting change in chemical reactivity: is the chemical activity of the reacting particles enhanced or suppressed by the complex formation? The question is not easily answered, and the answer cannot be general or unique. It depends on two factors of fundamental importance: 1) is the complex located on the correct reaction coordinate, and 2) how often do the reacting particles pass over the energy barrier in the direction of the reaction coordinate, and is the transition adiabatic or non-adiabatic. Many examples of activation and of passivation of chemical species by complex formation have been

reported; in some cases partial rules (applicable only to some types of reaction) have been established, but there are as yet no general principles allowing the reliable prediction of complex formation and reactivity effects.

These comments are equally applicable to solvation effects. The solvation concept is a more general one, and includes electrostatic effects as well as complex formation effects. The contribution from electrostatic interactions to chemical reactivity is not yet fully understood. There is evidence that the contribution has often been overstated, since chemical reactions between particles (even charged) are mainly short-range effects, involving exchange interactions rather than long-range Coulombic forces.

Being chemical methods of controlling the chemical reactivity of particles, complex formation and solvation often affect the mechanism of chemical reactions by varying the composition of the reacting species (free ions or ion pairs, radicals and their complexes, molecules and molecular associations, isolated atoms and clusters, etc.). The term reaction mechanism denotes the succession of elementary chemical processes which convert the initial substances into the final products. The mechanism is usually identified from the composition of the final and of the intermediate products, from the kinetics of disappearance of the reacting particles and of the formation of intermediates and products, from the composition of the intermediate active species (detected by physical methods), etc. We now have fairly reliable methods, indications, and criteria for establishing reaction mechanisms, but in general the formulation of a reaction mechanism in full detail remains a difficult problem which is only rarely (and not always unambiguously) solved.

Finding the mechanism is not an end in itself: it is a necessary stage in the determination of the rate-limiting step and in identifying the principal and the secondary reaction paths. The final aim is to find an effective method of controlling the chemical process and of increasing its yield and selectivity. Thus the identification of the mechanism is an important step forward towards the creation of highly selective, fast, and low-energy chemical technologies.

The discussion so far has been limited to chemical methods of controlling reactions; physical methods of stimulating and controlling chemical reactions involve the transfer of energy into the internal degrees of freedom of the reactants in an amount sufficient to overcome the energy barrier. Exposure to light, radiolysis, and plasmas are all physical methods of stimulating reactions by injecting energy into the electron shell. In most cases the electronically excited species thus formed have a high reactivity and react almost with a zero activation energy. However, this method of stimulating reactions has the following disadvantages: firstly, electronically excited states can react differently from the ground state, and therefore physical stimulation is often accompanied by a change of mechanism and a change in the composition of the final products; secondly, in the vast majority of cases the energy transfer process has a low efficiency, and only a small fraction of the energy supplied to the system is used in the chemical transformation.

Infrared lasers can pump energy into vibrational degrees of freedom, and they are often used to stimulate chemical reactions. This work has attracted a great deal of interest in recent years, and it has been shown that vibrational excitation is effective in overcoming the endothermic part of an energy barrier while having almost no effect on barrier crossing in thermally neutral or exothermic reactions. Thus the laser dissociation of molecules and the associated methods of isotope separation are now well established. These are endothermic processes, involving the energy pumping of vibrational levels. In neutral or exothermic reactions the utilisation coefficient of the vibrational energy to give chemical reaction is not more than 1–2%.

Mechanical activation can be an important source of stimulation in chemical reactions (for example, process in shock waves, at high pressures, under conditions of shear deformation, etc., see section VI). We know that mechanical deformation produces unusual chemical reactions, accompanied by luminescence, electron emission, and electric discharges. Similar effects are observed in phase transitions and structural rearrangements in crystalline solids. An unusual phenomenon was discovered recently: low-temperature "explosions", in which the elastic energy stored in glasses at low temperatures induces fast chemical reactions at temperatures below the boiling point of liquid helium. The paths and the physical principles by which the mechanical energy is converted into chemical energy are not yet understood, and their identification is an important problem whose solution may stimulate the development of new technologies and of a new type of chemical energetics (section VII).

As well as being energy-forbidden, chemical reactions can be forbidden in respect of the angular momenta of the reacting particles. This quantity must be conserved, and reactions involving a change in angular momentum are forbidden: only reactions not accompanied by a change in angular momentum are allowed.

Many chemical reactions require a change in orbital angular momentum; however, the orbital momentum rule is not rigid, since this momentum is strongly coupled to the motion of the molecule as a whole, and is transferred to external degrees of freedom. The rule with respect to spin angular momentum is much more strict: this appears in reactions involving free radicals, in the reactions of triplet molecules and ions, and in many other reactions involving paramagnetic species. The recently discovered magnetic effects in chemical reactions are the physical result of the spin angular momentum rule. They include spin polarisation of electrons and nuclei, the effect of external magnetic fields on the reaction, the magnetic isotope effect, and radio-frequency emission in chemical reactions. These newly discovered properties of chemical reactions involving radicals open new approaches to the control of reactions by using d.c. magnetic fields, or radio-frequency and ultra-high frequency electromagnetic fields, to influence electronic and nuclear spins and to remove the spin angular momentum rule. This new branch of chemistry (we could call it "spin" chemistry) is developing rapidly, and recent progress in this area has resulted in new methods of studying chemical reaction mechanisms and in the formulation of chemical radiophysics and of new principles for separating nuclear isotopes and isomers.

## IV. MOLECULAR AND SUPERMOLECULAR ORGANISATION OF CHEMICAL PROCESSES (MOLECULAR DESIGN)

The vast majority of chemical reactions used in industry and in science belong to the "non-organised" type, i.e. the participating species react through collisions which are random in time, in location, and in the mutual orientation of the particles. In other words, there is no molecular or supermolecular organisation of the chemical interaction in space and time.

On the other hand in molecular biology an entirely different situation exists: molecular and supermolecular organisation is a characteristic property of biochemical processes (for example, the synthesis of proteins, the transport of ions and other substances through membranes, electron transport along a chain of cytochromes and the associated phosphorylation, photosynthesis, enzyme catalysis, etc.). Enzymes can bind and orient the reagents, and thus organise the elementary

chemical acts and produce a high level of stereospecificity, reagent selectivity, and selectivity of reaction type, of localisation of the reaction, of temperature and pH, etc. In biochemical processes not only the elementary acts but also whole cascades of reactions are organised: for example, in photoreception processes each light quantum absorbed by the retina in the eye triggers a large cascade of chemical reactions which produce (in quantum yields up to $10^4$) cyclic guanosine monophosphate, producing an electric potential in the membrane which later appears in the brain as the result of the light perception. Because of their high level of organisation biochemical reactions achieve a selectivity, functionality, and operating speed which cannot be matched by ordinary chemical reactions.

Examples of supermolecular organisation of processes in cheimstry are still few. An unusual example is the interaction of methyl radicals with palmitic acid ($C_{16}$). In ordinary, "non-organised" chemical processes the most reactive site in the molecule is the $\alpha$ position, adjacent to the carboxylic acid group. On the other hand if the molecules of the acid are organised as a two-dimensional layer on a water surface the attachment of methyl radicals (formed by an electrical discharge or by irradiation of methane in the gas phase) takes place at the "tail" of the molecule and is accompanied by an increase in the length of the molecular chain (forming the $C_{17}$, $C_{18}$, etc. acids). This is a striking example of the molecular organisation of an ensemble on the reactivity (and even the direction) of a chemical reaction. This reaction is believed to have played an important role in the chemical evolution of life on Earth, since it can account for the synthesis of the initial substances used in the construction of biological membranes.

The simplest method of supermolecular organisation in chemical reactions relies on the use of molecular beams to deposit the reacting layers according to a given programme (layer thickness, periodicity, etc.) in order to prepare chemical compounds and compositions. In particular, this principle can be used to produce semiconductor structures and solid-state superstructures—crystals grown by depositing semiconductor layers a few atoms thick with a strictly periodic alternation of *n*- and *p*-type doping. These new materials offer a unique set of electrophysical properties and now have an important place in semiconductor technology and solid-state physics. Their preparation by the ordinary methods of "non-organised" chemistry would be impossible.

The structural elements which determine the molecular and supermolecular organisation of chemical processes could be micelles, vesicles, adsorbed monolayers, molecular membranes, clathrates, liquid crystals, clusters, interfacial boundaries, etc. There are known examples of the use of these structures in chemistry (interfacial catalysis, catalyst immobilisation, etc.). In these systems space–time organisation and periodic oscillations in properties are possible. For example, in the water–oil system in the presence of surface-active substances we observe oscillations in pH and in the electrochemical potential similar to those which occur in nerve cells, muscular tissues, and in mitochondria. Other examples of space–time organisation in chemical processes is the periodic precipitation of a solid product during the mixing of two substances (Liesegang rings), the Belousov–Zhabotinskii periodic reaction and its many analogues, the self-oscillations in the rate of many heterogeneous catalytic reactions, etc.

Many important processes cannot be carried out in the framework of conventional ("non-organised") chemistry. Thus, the photosensitised dissociation of water into hydrogen and oxygen (abiogenic photosynthesis, see section VII) requires three elementary stages: photo-generated charge separation, i.e. the formation of spatially isolated electrons and holes, the interaction of the electron with a water molecule (and reduction of the water to hydrogen), and the interaction of the hole with a water molecule (and oxidation of the water to molecular oxygen). The process must be organised so as to prevent the recombination (annihilation) of the electron and the hole, and therefore the reduction and the oxidation of the water must take place on different catalysts.

An example (perhaps not the best) of the molecular organisation of this process is shown in Fig.3. The catalysts are deposited on opposite sides of colloidal particles of the semiconductor $TiO_2$ (metallic platinum and ruthenium oxide). The photo-excitation of a sensitiser S results in its ionisation, and an electron is transferred to the $TiO_2$ either directly or through the intermediate carrier R. The electron then migrates into the conduction band of the $TiO_2$, it reaches the Pt, and it reduces a water molecule on the platinum. The hole migrates to the $RuO_2$ and oxidises the water to oxygen on this catalyst.

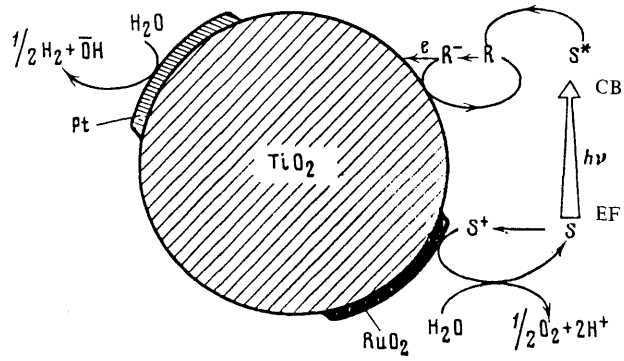



**Figure 3.** Organisation of abiogenic photosynthesis: EF is the Fermi level, CB is the conduction band.

This very simple version of an organised chemical system actually works, but its efficiency is low because of the many possible side-reactions. Clearly, a more perfect organisation is needed: the basic approach to the solution of the abiogenic photosynthesis problem is to seek a suitable organisation.

The development of organisational principles and the creation of organised chemical systems simulating biochemical systems (biomimetic systems) are among the most general and promising lines of attack used in modern chemistry, and the first tentative steps have already been taken (with some success) in this direction. A good example of a biomimetic system is provided by the calyxarenes (cyclic products of the alkaline condensation of phenols with formaldehyde, Fig.4). These molecules have a very unusual structure: the benzene rings with their substituents are arranged to form an enclosed space, so that the whole molecule is reminiscent of a vase (and is named from the Greek *calyx*, a vase). This "molecular vase" can have closed walls [in the form of a truncated cone, with a base consisting of the hydroxy groups (Fig.4*c*)], or the walls may be partly open if some of the benzene rings are folded outwards, forming windows in the wall of the vase (Fig.4*d*).

Because of their special structural organisation the calyxarenes can transfer metal ions through hydrophobic membranes, and they are superior even to crown ethers as carriers. Adding various functional groups to the calyxarene molecules produces catalytic properties simulating those of enzymes.

For example, the calyxarene whose structure is shown in Fig. 4*e* is a model of the enzyme aldolase and has the characteristic functions of this enzyme. We know that similar biomimetic properties are found also in some other molecules (for example, the cyclodextrins, which form inclusion compounds in which the chemical transformations of the substrate take place).

The most obvious supermolecular organisation effects are found in chemical reactions taking place in crystals. In the case of molecules organised as a crystal the intrinsic reactivity

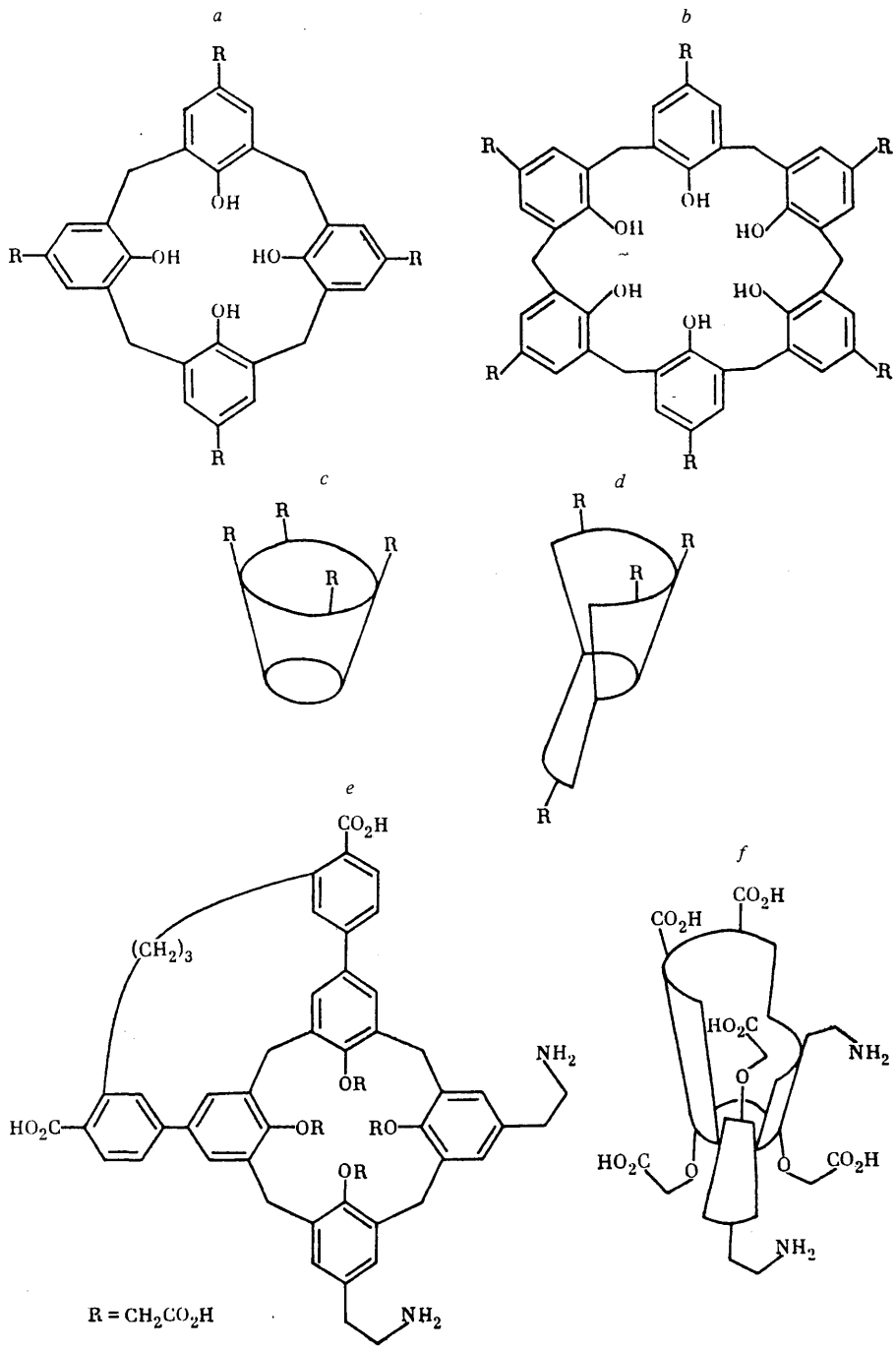
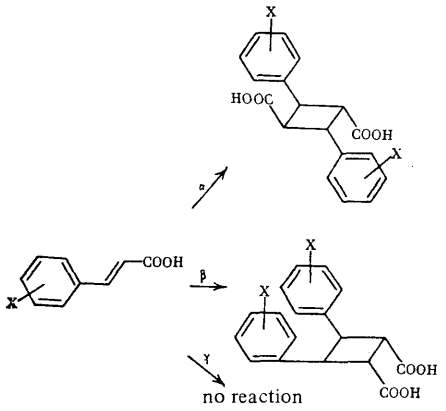



Figure 4. Structural formulae of some calyxarenes and diagrams of their three-dimensional organisation: calyxarene with four (*a*) and six (*b*) benzene rings; the wall of the cavity in calyxarene *a* can be closed (*c*) or partly opened (*d*) through the rotation of one of the four benzene rings; simulation of the function of the enzyme aldolase (*e*) and diagrams of its three-dimensional organisation (*f*).

(determined by the structure of the electron shells) is less important to the course of the reaction than the method by which the molecules are packed and stacked in the crystal. The direction of the reaction is determined by the intermolecular distances in the crystal, by the mutual orientation of the molecules, and by the three-dimensional symmetry of this crystal.

The features of solid-state reactions are clearly seen in the photodimerisation of *o*-ethoxy-*trans*-cinnamic acid:




The α form of the acid crystallises from acetone; it has a centre of symmetry, and neighbouring molecules are packed in a head-to-tail configuration. The product of the photodimerisation is a centrosymmetric molecules which retains the elements of symmetry of the initial pair of monomer molecules. The β form crystallises from benzene; the crystal has a plane of symmetry and the molecules are packed in a head-to-head configuration. The photo-dimerisation product retains the symmetry elements of the initial pair. The distances between double bonds are 3.6–4.1 Å in the α form and 3.9–4.1 Å in the β form. The stacking of the molecules is shown in Fig. 5 for one of the crystal projections; here R denotes the $C_2H_5OPh$ group, and the black rectangle the $CO_2H$ group. The γ form crystallises from aqueous ethanol solution; in this form the stacking of the molecule is unfavourable to the reaction (see Fig. 5), the distance between double bonds is 4.2–5.1 Å, and no reaction takes place.

The polymerisation of substituted diacetylenes (Fig. 6) to give conjugated polymers (organic semiconductors and organic metals, see section V) is determined by the same topological relationships between the structure of the crystals of the monomeric molecule and that of the crystals of the product. The monomeric molecules are organised in the crystal in such a way that only a slight rearrangement of the crystal structure is needed for the polymerisation. The dimer $(NS)_2$ is polymerised in the crystal in a similar way, giving the superconducting polymer $(SN)_x$ (see section V).

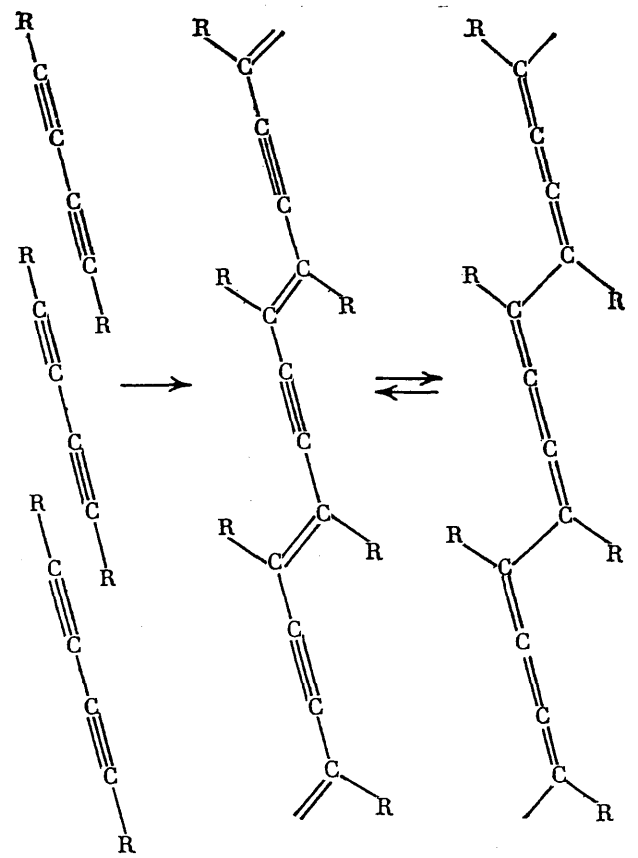


**Figure 6.** Arrangement of the molecules of diacetylene in the crystal and conversion into a conjugated macromolecule.

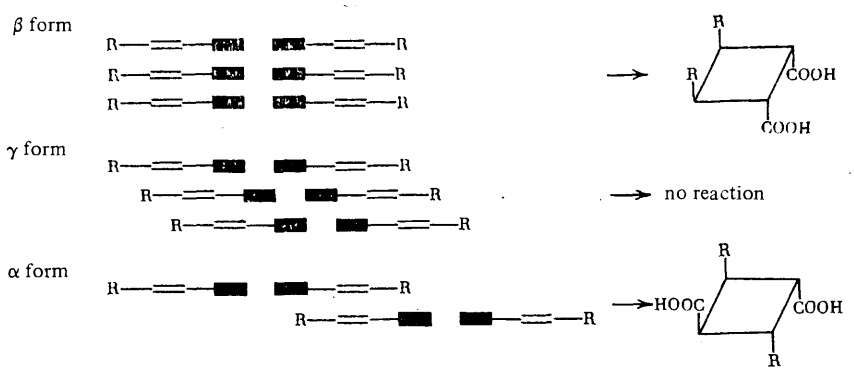



**Figure 5.** Arrangement of the molecules of *o*-ethoxycinnamic acid in the crystal and corresponding types of chemical reaction.

Pure optically active polymeric structures can also be obtained by the same method through the polymerisation of enantiomeric monomers in their crystalline form.

Crystal structure also allows topochemical control of the photo-induced transfer of a hydrogen atom to the keto group and to the C=C double bond. In the first case only the transfer of hydrogen atoms at a distance of 2.26–2.58 Å from the oxygen atom is allowed, i.e. at a distance smaller than the sum of the van der Waals radii of the H and O atoms (2.72 Å). In the second case atoms at a distance of 2.6–2.89 Å from the carbon atom of the double bond are transferred (again, at a distance smaller than the sum of the van der Waals radii of the H and C atoms, 2.90 Å).

Photo-dimerisation, oxidation ozonolysis, halogenation, and dehydrochlorination reactions also take place with a high stereoselectivity in crystals and on their surfaces. Many examples of extreme selectivity and topological control have been observed for reactions in crystals but not for the same reactions in solutions or in melts.

The organisation of molecules in crystals offers new possibilities of controlling the reactivity of a system and new pathways in synthetic chemistry. Many crystals display a high degree of polymorphism. Thus, methanol can crystallise in two forms (α and β) differing in the symmetry of their unit cell: cinnamic acid (discussed above) has three forms; more than 30 crystal forms are known for crystalline sulphur; many organic substances have several (up to 10 or 12) crystal-chemical modifications. We are eftectively discussing a new branch of chemistry: crystal-chemical engineering, whose objective is the construction of crystals matched to specified chemical programmes.

The molecular and supermolecular organisation of ensembles of reacting molecules (or, in other words, the supermolecular design of chemical reaction) is an important new principle for the control of chemical processes and a valuable asset of chemical engineering. So far this principle has not been fully explored, and few applications have been reported, but we can expect "organised" chemistry to play a leading role in chemical science and technology in the near future.

## V. CHEMICAL MATERIALS SCIENCE

Chemistry is the main source of materials for all areas of science and technology, from electronics and metallurgy to agriculture and medicine: in this sense chemistry genuinely stands at the centre of science. The development and evaluation of new substances, preparations, and materials, and the improvement of known or currently used materials, are the principal aims of modern chemistry. Its constituent elements are the synthesis of new substances and materials, the study of their properties, and the analysis of their behaviour under the conditions and regimes to which the materials will be exposed in practical applications. These topics can be combined under the general title of chemical materials science.

A traditional and ever-present problem is the development of highly stable inorganic materials: glasses and vitreous-crystalline materials (glass ceramics and ceramics). Important advances have been made in these topics, including the production of high-quality optical, heat resistant, and semi-conducting glasses with a high mechanical strength, thin-film and lamellar glasses with a high elasticity and thermal and dielectric strength, etc. Porous glasses with pores and channels of a given size (down to 10 Å or less) have been developed for use as filtering media (in particular, in the filtration of biomolecules, viruses, etc., and in the preparation of pure microbiological cultures).

New types of ceramic with a high mechanical, chemical, and dielectric strength have been obtained. These have a low thermal expansion coefficient, and they are widely used in technology, electronics, and radio. Metallic glasses have also been prepared: amorphous, vitreous metals with a high chemical stability and corrosion resistance.

Inorganic composite materials consisting of fibres in a metallic or ceramic matrix offer very attractive prospects. They can satisfy two apparently incompatible requirements: high strength and high crack resistance. For example, the boron-aluminium composite developed at the Solid-state Physics Institute of the USSR Academy of Sciences has a strength of 100–150 kgf $mm^{-2}$ (in the armouring direction), an elastic modulus of ~25000 kgf $mm^{-2}$, and a density of 2.7 g $cm^{-3}$, i.e. it combines the mechanical properties of a good quality steel with the density of aluminium. Ceramic fibre composites have a work of fracture an order of magnitude greater than that of the best homogeneous ceramic, and they can be used to produce light-weight components able to withstand hostile mechanical and thermal conditions.

Problems currently studied still include the development of corrosion-resistant alloys and materials, of inorganic semiconductors, photoresists, light detectors and photoelectric energy converters with a high quantum yield and a high selectivity and sensitivity towards chosen regions of the optical spectrum, and the development of piezoelectric, ferroelectric, and other materials for acousto-electronics.

Improvements are being sought in mineral fertilisers of high food value, assimilability, and optimum composition, in new rubbers based on polyurethanes and polysiloxanes, fluororubbers, etc., offering a high thermal and chemical resistance, frost resistance, and good elastic and relaxation properties, in new plastics, resins, and ion-exchanger materials and adsorbents, in long-life lubricants and viscosity additives, in lacquers with a high adhesion and high-grade electrical insulation and anticorrosion properties, in glues, sealants, and surface-active substances and coatings, in porous and filtration media for separating and purifying substances in the food industry, in technology, and in medicine, and in strong fibres (both synthetic and modified natural fibres), etc.

The development improved or new pigments, phosphors, scintillators, and laser generation materials is a continuing problem. Light-fast dyes are needed for optical lasers, laser shutters, and modulators. New substances are being developed for chemical light sources (substances which resemble luminol in converting chemical energy into light energy with a high efficiency).

Polymer materials and their most recent modifications (polymer composites) occupy an important place in modern materials science. Current developments include various composites reinforced with organic or inorganic fibres (glass, boron, asbestos, graphite, and carbon fibres, and fibres based on boron nitride, $TiO_2$, $Al_2O_3$, etc.). This wide variety of composites offers a wide range of useful properties: electrical strength, chemical stability, elasticity, mechanical strength in shear and compression, resistance to plastic flow, etc. Further substantial improvements in the mechanical and thermal strength of these composites can be expected when the fundamental problem of lowering the concentration of localised stresses at the fibre–polymer matrix interface has been solved. Various approaches to this problem are being studied: for example, by inserting a boundary layer with an elastic modulus intermediate between those of the fibre and of the matrix, or by applying artificial elastic deformations to the boundary to suppress (or compensate) the main stresses generated between the fibre and the matrix. The same problem arises in the development of high-strength inorganic composites.

Dispersion-strengthened or filled (usually with an inorganic filler) polymer materials are similar to polymer composites. With all these materials the material production stage can be by-passed, and the article can be formed directly, but this requires a very precise and reliable control over the properties of the chosen composite.

Other important materials include incombustible or fire-resistant coatings and cloths, and anti-static materials for use in situations where electrification or static electricity can present sanitary, explosion, or fire hazards (floor coverings in computer rooms or in medical X-ray rooms, materials for protective clothing in tanker fleets, in the petrochemical and gas industries, etc.). Light and cheap (preferably organic) materials are also needed for protecting electronic and radio equipment from stray electromagnetic fields, and for absorbing electromagnetic radiation.

Methods of preparing entirely new materials (organic semiconductors and metals) have been discovered in recent years. Their precursors were the polymers with a conjugated $\pi$-electron system (polyacetylene, polyphenylene, etc.), prepared by polymerising the appropriate monomer in solution; these were amorphous substances with a high concentration of defects, a low electrical conductivity, and a poor chemical stability towards oxygen and other reagents. An important step forward was made by the production of perfect (almost defect-free) conjugated polymers by polymerising the monomers in crystals (see section IV). Another success was the discovery of ways of modifying the conduction properties of organic semiconductors by treatment with bromine, iodine, $AsF_5$, or inorganic salts: this operation (doping, or alloying) creates local impurity centres in the semiconductor structure and results in a large increase (by 10–11 orders of magnitude) in the concentration and mobility of the charge carriers and therfore also in the conductivity of the material. This type of doping converts polyacetylene (for example) into a substance with an almost metallic conductivity. Furthermore, thin films of these conjugated polymers prepared by polymerising the monomer in a crystal offer unique and reversibly controllable thermal and optical properties.

Organic batteries and accumulators with potentials up to 4.5 V and capacities up to 300 W $kg^{-1}$ have been produced from doped conjugated polymers. According to estimates made in the USA the scale of production of organic semiconductors (for electronic applications only) was 10000 tonnes in 1981, and had doubled by 1984. They are used in electrical noise suppression systems, in cable sheaths, in accumulators and current sources, in photovoltaic apparatus and converters, and in micro-electronic circuits. Further improvements can be expected, and the new materials with improved electrophysical properties have a promising future.

A good example of a successful development in chemical materials science is the discovery of an entirely new type of substance: organic metals. These are organic compounds with a crystalline molecular organisation which results in a high electronic conductivity (up to $10^5\ \Omega^{-1}\ cm^{-1}$), approaching that of the best metallic conductors (for example, mercury). Typical materials of this type are the ion-radical salts, in which the cation is a radical such as tetrathiafulvalene (TTF), tetraselenafulvalene (TSF), tetramethyltetraselenafulvalene (TMTSF), etc., and the anion is a radical such as tetracyanoquinodimethane (TCNQ) or its dimethyl derivative (DMTCNQ), or an inorganic anion ($PF_6^-$, $AsF_6^-$, etc.). In crystals of these compounds the cation radicals are stacked with their planes in a parallel orientation, forming small stacks (one-dimensional chains in which strong interactions between the electrons of the $\pi$ system develop, producing a high electrical conductivity). The anions are also arranged in one-dimensional chains, parallel to the cation chains (the molecular organisation of these crystals is discussed in detail in section II).

Organic metals have a high electrical conductivity (up to $10^3\ \Omega^{-1}\ cm^{-1}$) even at room temperature; at lower temperatures their conductivity is still higher. For example, it is $10^5\ \Omega^{-1}\ cm^{-1}$ for $(TMTSF)^+(DMTCNQ)^-$ near 40 K, and $10^4\ \Omega^{-1}\ cm^{-1}$ for $(TMTSF)^+(ClO_4)^-$ at 50 K. The one-dimensional packing of the conducting cation chains results in a highly anisotropic conduction: the ratio of the conductivities along and across the chains is 500–1000.

The behaviour of the organic metals includes two surprising features. The first stems from the instability of the one-dimensional chains, predicted by Peierls in 1954, and consists in a change from a uniform distribution to an alternation of intermolecular distances at low temperatures, producing waves of charge density (or spin waves in the case of chains of paramagnetic particles). Because of the alternation of intermolecular distances in the one-dimensional chain the energy band containing the levels of the valency $\pi$ electrons splits into two systems of levels: a lower system, filled with electrons, and an upper, empty system. In order to cause conduction we must transfer an electron from the filled into the empty system, i.e. we must surmount the energy barrier separating the full and the empty band. It follows that at low temperatures (below the Peierls transition temperature) the organic conductor becomes a semiconductor (or even an insulator if the energy gap between the two bands is wide enough). Among the organic metals we find many compounds which become superdielectrics at low temperatures (12–180 K), with a dielectric constant $\varepsilon \cong 3000$ and a strong anisotropy ($\varepsilon_\parallel/\varepsilon_\perp \cong 500$).

Another surprising property of the one-dimensional organic metals is their transition to the superconducting state, first discovered in 1979 for the compound $(TMTSF)_2^+(PF_6)^-$: at 0.9 K and 12 kbar pressure this organic metal is converted into a superconductor. It was later shown that other salts of composition $(TMTSF)_2^+X^-$, where $X = AsF_6$, $TaF_6$, $SbF_6$, and $ReO_4$, become superconductors at low temperatures and high pressures; the salt $(TMTSF)_2^+(ClO_4)^-$ is a superconductor at 1.2 K even under normal pressure.

The superconductivity mechanism in organic superconductors is still not clear. The formation of Cooper electron pairs and their organised motion in the superconducting state may be controlled by coordinated vibrations of the lattice, and in particular by vibrations of the anion chains (as in classical metallic superconductors). However, a different mechanism (proposed by Little in 1964) is also possible: the motion of the Cooper pairs is controlled by waves of electron polarisation travelling along the side chains. The classical mechanism of superconductivity seems the more likely to apply to the organic metals so far synthesised.

Many inorganic and mixed salts have also been shown to have a near-metallic electrical conductivity. They include the platinum salts $K_2Pt(CN)_4Cl_{0.3}\cdot 3H_2O$ and $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$, the mercury salts $Hg_{3-\delta}AsF_6$ and $Hg_{3-\delta}SbF_6$ (where $\delta = 0.14$), and also sulphonitride $(SN)_x$, a polymer with metallic conduction. The last three compounds also show superconductivity. The molecular organisation of their crystals is discussed in section II.

Synthetic organic metals, superdielectrics, and superconductors have only recently come to the fore in science: their discovery has created an entirely new field in materials science, with attractive prospects. This field includes some unusual magnetic materials: organic ferromagnetics, whose synthesis is being intensively studied at present.

Chemistry plays an important role in agriculture and medicine. The chemical problems in these areas are fundamental: creating new and effective medicinal preparations (in particular, anticarcinogens), immobilising drugs and immunological

substances on the macromolecules of synthetic or natural polymers in order to increase their effectiveness and to extend their useful life, and developing pesticides, agricultural chemicals, pheromones, and other biologically active compounds. This group of topics includes the development of gel polymers and of synthetic polymeric materials for artificial organs used in surgery, and the modification of their surface to produce antithrombogenic properties. Another important problem is the development of artificial blood substitutes (for example, the perfluorohydrocarbons, which are chemically passive, have no metabolic activity in the organism, and offer a high oxygen capacity, recently shown to be due to complex formation between the oxygen and the fluorine atoms of the fluorinated molecules.

Even this list of materials is not exhaustive, and it is being continually extended. Because of the rapid developments in technology and in the adjacent scientific areas it is difficult to predict which materials will be most widely applied in the near future: it is important for all chemists to remember that the creation of new substances and materials is the fundamental aim of chemistry, and that all their efforts should continue to be devoted to the achievement of this aim.

## VI. CHEMICAL TECHNOLOGY

The previous section dealt with existing and likely future developments in chemistry: we shall now consider the methods by which these developments can be realised, i.e. we shall discuss new methods and new principles in chemical technology. Improving existing technologies and developing new technologies is one of the main responsibilities of chemical science. Simplicity, dependence on few stages (preferably, one stage), reliability, moderate energy requirements, high operating speed and yield, continuous operation, absence of residues, acceptance of untreated raw materials, these are the main criteria to be aimed at in new technological developments.

Undoubtedly the central place among the new technologies belongs to catalysis. At present 85% of all industrial processes, responsible for 70% of all chemical production, are based on catalysis. Processes offering a high selectivity and operating speed, economically attractive, and with low energy requirements can be discovered and developed only by using catalysis. This state of affairs has traditionally been found in both heterogeneous and homogeneous catalysis. Significant advances have been made, and many highly effective processes have been adopted by industry, but even greater prospects are seen in advances whose application is still awaited. These include metal-complex catalysis, which allows many reagents to be converted directly into the wanted products without intermediate synthetic stages. For example, the carbonylation of methanol to give acetic acid can take place on rhodium complexes with a methanol selectivity of 99%, and the oxidation of ethylene to acetaldehyde on palladium catalysts has a selectivity of ~95%. Highly effective processes of hydroformylation, the direct synthesis of aromatic isocyanates from nitroaromatic compounds, the synthesis of vinyl acetate from ethylene and acetic acid, and other valuable processes have been developed. The high selectivity of metal complex catalysis is found also in electrochemical processes (for example, the electrochemical oxidation of olefins in the presence of osmium salts gives an almost 100% yield of glycols).

The phenomenon of catalytic metathesis is being studied as a path to the industrial production of new organic compounds and new materials, especially macrocycles, and unusual substances like catenanes (cyclic molecules whose rings are "threaded" through each other like the links of a chain). The synthesis of a catenane from a cyclic diene can be represented schematically as follows:



The first stage is the formation of an inner loop which then becomes fixed by a metathesis reaction; the final result is a catenane.

In another interesting development catalytic processes are conjugated so that the energy evolved by one reaction is used to stimulate another. This possibility exists both in heterogeneous and in homogeneous metal complex catalysis. A good example of conjugated catalytic reactions in cells is the synthesis of ATP by the oxidative phosphorylation of ADP followed by the use of the energy evolved in this reaction to stimulate energy-deficient reactions (including "difficult" reactions such as the biological reduction of molecular nitrogen).

The metal-complex catalysts in the present state of development have a number of shortcomings which can partially (or, on occasions, wholly) offset their advantages. The most serious of these is the need to generate a molecular organisation for the catalyst which ensures long-lived operation of each active centre without decomposition, coupled with ready access of the reacting species to this centre and easy removal of the reaction products. The following principles are being studied as a means of achieving this organisation: the immobilisation of the active centres on the surface of a solid, the "clusterisation" of a group of active centres on solid surfaces (an approach which almost totally eliminates the distinction between homogeneous and heterogeneous catalysis), and the introduction of active centres into the molecular structure of organic crystals (for example, between the planes of carbon atoms in graphite).

A promising approach is the immobilisation of homogeneous complex catalysts in gel polymers, i.e. the chemical or quasi-chemical bonding of the catalyst to a macro-molecule. The immobilisation principle is very close to the operating principle of natural enzymes, which consist of metal-organic catalysts incorporated in the structure of protein macromolecules and whose economy and efficiency are unrivalled. This principle of catalyst organisation offers one fundamental advantage: it can be applied to processes which require the participation of several active catalytic centres (as in the enzyme nitrogenase, in which two active centres contribute to the reduction of nitrogen). The immobilisation of active centres on macromolecules followed by control of the molecular conformation can be used (if necessary) to produce "many-centre" catalysis.

The immobilisation principle is often treated as an enzyme modelling principle: this is a very important and forward looking new attitude in chemical research. A closely related and actively investigated topic is catalysis on immobilised enzymes, which offers attractive prospects in artificial food technology (the synthesis of proteins, aminoacids, and glucose), in medicine, in the chemical analysis of biologically active compounds, in immunology, in micro-energetics (especially in fuel cells, see section VII), and in organic synthesis. Though this work is still on a modest scale because of the high cost of enzymes, current developments in biotechnology and genetic engineering should make enzymes more accessible and increase their "practicality", thus leading to the adoption of immobilised enzymes as an important element of the chemical technology of the future.

Catalysis should play an important role in the new technologies of natural gas and petroleum treatment to give valuable chemical products: the key element in these processes will probably be the catalytic activation of saturated hydrocarbons (especially methane). In view of the world shortage of

energy, great interest is shown in the development of low-energy and high-yield technologies for the treatment of solid fuels (coal, shales, peat, wood cellulose, etc.), aimed at producing hydrogen, carbon monoxide, and artificial petroleum and petrochemicals.

An equally pressing problem is the treatment of inorganic raw materials (ores and minerals). We require improved flotation techniques, more selective flotation reagents, and extractants offering a more quantitative separation of non-ferrous and rare metals and of fluorine and other elements. Chemical methods of metal extraction have long been used in metallurgy (for example, the cyanide method of gold extraction), but their importance is now increasing because of the exhaustion of the richer ores. New technologies can be developed on the basis of organic compounds such as complexones and extractants which react selectively with the ions of the given metals and transfer them from the complex ore into the solution. We could witness the development of a new branch of metallurgy: solvato-metallurgy, differing from traditional metallurgy in not requiring energy-wasteful melting processes.

"Microbiological" metallurgy offers even more attractive prospects. It is based on the ability of some micro-organisms to "treat" ores and selectively extract certain metals from them. These chemolithotrophic (literally, "rock-eating") micro-organisms live in water and they obtain their life-supporting energy from the enzymatic oxidation of inorganic substances, thus "freeing" the metal from its ore and transferring it to the aqueous solution. The large-scale microbiological production of copper is already carried out in several large mining concerns; in the USA more than 10% of the copper production uses this method, and uranium production by the same method is planned. In principle, cultures of micro-organisms which selectively "produce" any wanted metal could be "grown" by genetic engineering: this approach is part of an important new scientific area, biotechnology, which seems likely to expand the possibilities of chemical technology on a vast scale.

Another important success of modern chemistry was the discovery of the reduction (fixation) of molecular nitrogen by homogeneous catalysts. We now await the corresponding development of an industrial nitrogen fixation technology offering a high operating speed and selectivity and a low energy consumption. A similar problem exists in respect of carbon dioxide: an inorganic raw material available in almost limitless quantities. Catalysis can be expected to play a key role in solving this problem. The catalytic utilisation of $CO_2$ for the synthesis of substances currently listed as "petrochemical" and expected to be in short supply in the very near future should be treated as a pressing chemical problem. Some initial work in that direction has already been reported: we know that the interaction of $CO_2$ with hydrogen on Ni, Co, and Ru catalysts gives methane, whereas methanol is obtained on oxide catalysts. There are also non-catalytic methods of fixation of $CO_2$, but they are much less cost-effective. For example, the electrolysis of an aqueous solution of $CO_2$ and sodium sulphate was shown to produce methanol (in these experiments the current source was a gallium arsenide solar cell).

Combustion processes play an important role in chemistry. They are mainly used in chemical energetics, to produce thermal and mechanical energy. The problem includes the combustion of gases in engines, and the gasification and combustion of liquid and of solid fuels. The main partner of the fuel in combustion processes is oxygen (free, or bound), and the main products are water and carbon dioxide. Combustion technology is continuously advancing, and wider applications are being found. These include mixing-chamber ignition in internal combustion engines, the organisation of combustion within the seam to improve the yield of petroleum deposits, underground gasification in coal mines, etc. All these problems are important, and no effort should be spared in seeking their solution.

Interesting new possibilities were recently identified in the use of combustion processes in industrial inorganic synthesis. A new type of heterogeneous combustion process, not involving oxygen, was discovered: the combustible material is a high-melting metal (Ti, Zr, Hf, Nb, Ta, etc.), and the oxidiser is a non-metal (B, C, Si, molecular nitrogen, hydrogen, etc.). Using combustion processes in these systems a new technology was developed: the self-propagating high-temperature synthesis of high-melting inorganic compounds and materials. The advantages of the technique include low energy consumption, high operating speed, the production of substances and materials having a prescribed composition, physicochemical properties, particle size, and porosity, high-purity products, simple technological design, and ecological purity.

The new technology is being rapidly assimilated in inorganic synthesis: it has already been used to produce more than 200 compounds, including carbides (TiC, ZrC, HfC, NbC, SiC, SC, $Cr_3C_2$, $B_4C$, etc.), mixed carbides (TiC–WC, TiC–WC–$Mo_2C$, TiC–ScC, etc.), nitrides (TiN, ZrN, NbN, TaN (cubic, and hexagonal), BN (cubic), AlN, $Si_3N_4$), single-phase solid solutions of nitrogen in Ti and Zr, borides ($TiB_2$, TaB, CrB, NbB, MoB, $MoB_2$, MnB, NiB, $LaB_6$, etc.), silicides ($MoSi_2$, $TiSi_2$, $Ti_5Si_3$, $SrSi_2$, $TaSi_2$, etc.), compounds of S and Se with Nb, Ta, W, Mo, V, Nd, and the mixed chalcogenides $WNbS_2$ and $MoNbS_2$, hydrides ($TiH_2$, $ZrH_2$, $NbH_2$, $ScH_2$, etc.), intermetallics (NiAl, FeAl, NbGe, NiTi, etc.), solid solutions of carbide nitrides of variable composition (TiN–TiC, TaC–TaN, NbC–NbN, etc.), and solid inorganic alloys and composites (TiC–$TiB_2$, WC–Co, $B_4C$–$Al_2O_3$, Vn–Fe, etc.). All these materials are refractory, super-hard, and wear resistant, and they are used in various areas of technology as hard alloys, abrasives, wear resistant and thermally stable coatings, high-temperature heating elements, alloy steels, fire-resistant materials, etc.

The physicochemical mechanism of this process (the motion of a high-temperature combustion region, leaving a trail of synthesis products, (see Fig.7) offers a number of additional technological possibilities, including the direct preparation of refractory articles of any shape without going through the material production stage; this facility avoids the difficult technological process of forming the refractory material into the desired shape. The new technology is being developed very rapidly because it has firm scientific foundations as well as offering attractive prospects.

Interesting effects have been observed in materials under the combined effects of high pressure and shear deformation: these conditions lead to a number of unusual reactions such as the formation of salts by the interaction of solid metals and solid organic acids, the polymerisation of benzene and other monomers which do not polymerise under normal conditions, the penetration of metal atoms into graphite through the reaction of graphite with solid metals, the formation of solid solutions from a mixture of metal powders, etc. These are apparently the conditions met in shock waves, though in the latter the non-isothermal compression and the shear deformation take place in times of $10^{-12}$–$10^{-6}$ s (as opposed to static conditions). Many unusual chemical effects take place in shock waves: the conversion of graphite into diamond, the synthesis of metal nitrides and of boron carbide and nitride, the polymerisation of benzene, etc. The further development and improvement of these technological possibilities is of great interest.

The creation of photochemical technologies such as photolithography is of definite (though specialised) interest. However, there are two problems of more general interest in which

photochemical processes play a major role: silverless photography and the fixation of solar energy (the latter will be examined in more detail in section VII, devoted to chemical energetics).

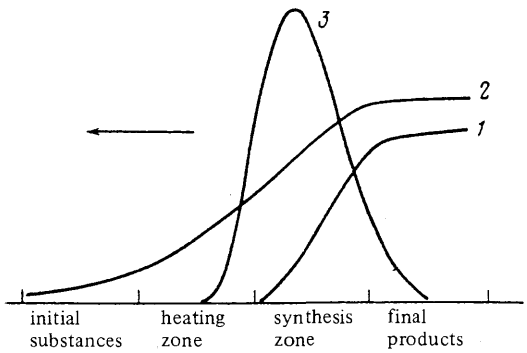



Figure 7. Motion of the combustion zone during self-propagating high-temperature synthesis: *1*) conversion, *2*) temperature, *3*) rate of evolution of heat; the arrow denotes the direction of the combustion wave.

The search for silverless light-sensitive materials and the development of new photographic techniques based on these materials have been stimulated not only by the world shortage of silver (though this is often quoted as the main incentive) but also by the special requirements of modern technology. Significant advances have been made in the synthesis of silverless photosensitive materials of various types (diazotype, vesicular, photochromic materials, etc.), which offer unique properties including high resolution, colour capability, absence of the development stage, reversibility of information recording, and the possibility of repeated use of the same photographic material. The most important problem still outstanding is to improve the light sensitivity of these materials (to the level of $10^7$ cm$^2$ J$^{-1}$ or better). Various suggestions have been made for increasing the quantum yield of the formation of the product responsible for the development of an image. These include the use of radical chain reactions (for example, photo-induced polymerisation), photostimulated phase transitions (for example, the crystallisation of an amorphous substance in the *cis* form stimulated by the presence of the *trans* isomer formed from the *cis* isomer under the influence of light), and catalytic reactions (for example, redox reactions of metal ions "set free" from inactive complexes by exposure to light). The latter include enzyme catalysis reactions: under the influence of light the enzyme is converted from an inactive into an active state, and the image-forming materials are produced as a result of the photo-activation. The term photoenzography has been applied to this new type of photography.

Silverless photography is being developed along several different paths at present, and the best approach has not yet been identified. Sensitisation, which offers higher sensitivity and wider spectral limits (as it does with silver-based photographic materials), is also being studied in conjunction with the new materials.

Plasma-chemical and laser-chemical technologies are also of interest, and have been applied in a number of processes. For example, some evidence of isotope separation by laser chemistry has been observed, but the yield of the method appears to be low. Radiation-chemical technologies are of far greater practical significance because of the large-scale construction of powerful nuclear reactors and of the on-going integration of chemical technology with nuclear energetics. Radiation chemistry has now penetrated the technology of rubber and resin cross-linking and modification, and is widely used in the production of plastics, polymers, and composites as well as in the sterilisation of medical products. Radiation-chemical techniques also offer attractive prospects in chemical energetics (see section VII).

Photochemical, plasma-chemical, and laser-chemical technologies occupy an important place in an important area of modern industry: microelectronics, and their potential applications in this area are still far from being exhausted. The technologies are aimed at the deposition of metallic, oxide, or semiconducting thin films and epitaxial layers by the thermal, photochemical, or plasma-chemical decomposition of metal-organic compounds in the gas phase or by the laser-chemical decomposition of the same compounds adsorbed on the surface. The advantages of this technology include a high purity of the product, relatively low operating temperatures, the possibility of depositing coatings of any type on any surface in any sequence, and generally good adhesion of the layers. Further advantages are the possibility of doping the semiconductors by decomposing metal-organic compounds with laser or electron beams, and the possibility of preparing photographic stencils and protective or diffusion masks without resorting to photolithography or to chemical etching. Similar technologies can be used to prepare super-pure metallic or semiconducting coatings, and magnetic materials (ferrites, magnetic tapes, etc.) with particles of micron or sub-micron size. Almost all the elements of microelectronics (conductors, resistors, semiconductors, dielectrics, microcircuit elements, or even the entire microcircuits) can now be prepared by these techniques.

Many of these processes have already been adopted by industry, but even greater technological possibilities remain to be exploited. The development and improvement of technological methods of using metal-organic compounds in microelectronics is a problem of the first importance. Together with organic semiconductors and metals, and their use in electronics (see section II), the use of metal-organic compounds in microelectronics is a new area of work which could be called organic microelectronics. This is yet another striking example of the integration of different sciences, leading to the birth of new technologies.

This integration has also produced a new and promising technology: the nuclear chemical synthesis of elements, which could be described as a modern "alchemy". We know that semiconductor devices require silicon of the highest purity, doped with phosphorus. The distribution of the doping element (i.e. of the phosphorus in the silicon) must be extremely uniform, and an adequate uniformity is difficult to achieve by chemical methods of doping. A brilliant solution of this problem relies on the fact that as a result of neutron irradiation a silicon atom absorbs a neutron and is rapidly converted into a stable phosphorus isotope by beta-decomposition. This process results in very uniform doping and has already been adopted on a production scale.

This is just one example of the "alchemical" introduction of a required chemical additive. The inverse problem (purification of a material) is also soluble in principle: this approach

replaces the multistage, complex, and expensive chemical purification by neutron irradiation, resulting in transmutation ("alchemical" conversion) of harmful impurities into harmless atomic species.

Nuclear-chemical technology has been used to synthesise a large group of chemical elements (for example, plutonium, technetium, and the entire transuranic group). Furthermore, in the case of some elements which are usually extracted from the atmosphere or from the earth by conventional techniques (for example, xenon, palladium, platinum) the nuclear-chemical technology could have economic advantages. The large-scale practical application of these technologies could have far-reaching economic consequences. Obviously, nuclear-chemical synthesis and its adoption in industry and in materials science will require a well coordinated effort from scientists in nuclear and neutron physics and in nuclear chemistry and radiochemistry. Chemists must be prepared to contribute to the development of this promising branch of modern (and future) chemistry.

## VII. CHEMICAL ENERGETICS

The development of effective methods of converting chemical energy into other forms of energy and the creation of chemical means of storing energy in high-energy substances are two areas being actively developed in present-day chemistry, which can be combined under the title of chemical energetics. Its place in modern energetics is still relatively modest, but some predictions of future energy requirements and of the energy structure of world economics (which we shall not attempt to analyse here) foresee an important role for chemical energetics in the future.

The development of methods of converting chemical energy into other forms of energy is one of the oldest problems known to mankind. For many thousands of years it had only one solution: the combustion of high-energy substances (fuels, such as coal, petroleum, gas, wood, peat, and shale). In spite of the very great technological progress in the organisation of combustion processes in order to maximise their efficiency this method remains economically the least attractive. The direct conversion of chemical into electrical energy (i.e. the combustion of the fuel in an electrochemical fuel cell) is a far more effective method of conversion. The development of electrocatalytic methods of combustion and of methods of raising the energy conversion efficiency in fuel cells is one of the fundamental problems in modern chemistry. Important advances have been made towards these goals, and electrochemical energetics are now applied in practice but on an industrial scale still too small to justify classifying the electrochemical approach as "large-scale energetics".

A special variant of the chemical fuel cell is the biochemical cell, whose operation depends on the use of immobilised enzymes to carry out oxidation–reduction reactions. For example, hydrogenase immobilised on a graphite electrode can oxidise molecular hydrogen, producing a hydrogen potential on the electrode. On a second electrode oxygen can be reduced to water by using an oxidase enzyme immobilised on graphite (for example, polyphenol oxidase). The combination of these two half-cells offers an ecologically clean biochemical fuel cell with a high efficiency. Of course, these cells also have some serious shortcomings (short life, the need to purify the fuel to avoid poisoning the enzyme, etc.), but their further development and improvement could be useful.

Among the other methods of converting chemical energy we should mention chemiluminescence, i.e. the generation of light in chemical reactions, and the generation of coherent radiation in chemical lasers.

Another important branch of chemical energetics is the development of cost-effective methods of producing high-energy substances such as hydrogen, methane, etc., which are convenient to use, easily transportable, and capable of storing energy for indefinitely long periods. The most important energy carrier of this type is hydrogen, whose purest (and practically inexhaustible) source is water. The production of hydrogen from water is a problem of strategic importance. Another equally important problem is the development of effective methods of utilising solar energy. These two problems are closely interrelated. We know that solar energy is an important source of energy, and that the only practical method of exploiting it in large-scale energetics is the development of photo-hydrogen energetics.

Various methods of obtaining photo-hydrogen from water have been described; the simplest is the electrolysis of water using electrical energy generated by semiconductor energy converters (Si, GaAs, CdSe, etc.). For a light conversion coefficient of 14% (the normal efficiency of modern silicon photocells) and a 70% utilisation factor of the electrical energy in the electrolytic cell we obtain an overall efficiency of ~10% in the conversion of solar energy into photo-hydrogen. This approach is still expensive and unattractive for large-scale application (the "bottle-neck" being the high cost of the semiconductor photo-converter), but it seems reasonable to devote further effort to it, and to examine (in particular) the possibility of using organic semiconductors.

An alternative approach is photoelectrocatalysis, i.e. the electrolysis of water on a semiconductor surface (for example, $TiO_2$) coated with a deposited catalyst (for example, metallic platinum). A hole-electron pair is generated in the semiconductor by photolysis, and the electron migrates towards the Pt where it reduces the water to molecular hydrogen, whereas the hole migrates towards the $TiO_2$ surface and oxidised the water to molecular oxygen. This approach is also relatively ineffective at present, but it has a promising future (through the selection of more suitable semiconductors, the modification of their surface, etc.).

The most attractive path to photo-hydrogen production at present is the third: the identification of molecular photocatalytic and photosensitised systems. It is the nearest approach to natural photosynthesis, which can be interpreted most simply as the photogeneration of an electron and a hole through a series of intermediate steps: the ultimate result is the reduction of $CO_2$ to carbohydrates (by the electron) and the oxidation of the water to oxygen (by the hole). The only difference between molecular photocatalysis and photosynthesis is that in the former the electron reduces the water rather than $CO_2$, and therefore the process is also called artificial (or abiogenic) photosynthesis.

These studies have met some serious problems, many of which have already been fully formulated and are being actively solved. The two most important problems in this area are: 1) to ensure the separation of the charges created in the primary photolysis act, so as to prevent their recombination by the inverse reaction, and thus to increase the efficiency of the photolysis; 2) to separate the secondary charge carriers and to prevent their premature recombinations (i.e. their annihilation) so as to ensure their participation in useful oxidation–reduction reactions with the water. Various methods of overcoming these problems have been suggested, all based on the specific attributes of the supermolecular organisation of the photoprocess (see section IV). In model systems both the half-reactions have been realised separately: the reduction of water to hydrogen and its oxidation to oxygen. There are also reports of the combination of these half-reactions into a single process, but we are still a long way from the creation of an effective and economically viable process.

Abiogenic photosynthesis is of interest also because of the possibility of exploiting visible light, whereas photoelectrolysis and photoelectrocatalysis on semiconductors offer a high sensitivity only with ultraviolet radiation, which is present only in small amounts in the solar spectrum.

The radiation-chemical method of producing hydrogen from water offers good prospects, especially in conjunction with high-temperature thermolysis. It relies on the joint application of radiation and heat from nuclear reactors. In the direct, low-temperature radiolysis of water the yield of hydrogen is low because of the reverse recombination of the hydrogen atom with a hydroxyl group. However, at high temperatures the yield of hydrogen increases as a result of the reaction

$$H+H_2O\rightarrow H_2+OH$$

To maximise the hydrogen yield we must remove the hydroxyl from the reaction system. This can be done by using an acceptor with a high effectiveness and selectivity towards hydroxyl: carbon monoxide, which reacts with hydroxyl as follows:

$$OH+CO\rightarrow CO_2+H$$

Thus in the presence of CO the process becomes a chain reaction, which often increases its effectiveness and the hydrogen yield. The overall balance equation for the chemical products is

$$H_2O+CO\rightarrow H_2+CO_2$$

In practice these conditions lead to the chain reduction of water to hydrogen coupled with the oxidation of CO to $CO_2$; chain initiation is radiation-chemical. The same process can be used for the direct conversion of carbon and water into hydrogen and carbon dioxide:

$$C+2H_2O\rightarrow CO_2+2H_2$$

Other thermodynamic cycles leading to the reduction of water to hydrogen are being studied at present: they all rely on the use of waste heat from nuclear reactors, and all can be classified as variants of hydrogen energetics.

Lastly, chemical energetics and the synthesis of high-energy substances should not be confined to the production of photo-hydrogen. We need to develop the principles by which chemical reactions can be coupled so that the energy evolved by one reaction can be utilised in a high-energy synthesis by another reaction (as in the well known synthesis of ATP and high-energy substances in coupled biochemical reactions). The realisation of these principles and of chemical systems based on them, resembling molecular heat engines, would be an important milestone in both chemical technology and chemical energetics.

Equally attractive is the prospect of the direct conversion of mechanical into chemical energy (for example, the direct mechano-synthesis of calcium carbide from the carbonate, or of hydrogen from water). The mechano-synthesis of high-energy substances is possible, in principle, through chemical reactions under pressure and in the presence of shear deformation (see section VI). Of course, the replacement of hydroelectric stations by hydro-hydrogen stations seems a flight of fantasy at the moment, but the prospect is entirely realistic and worthy of scientific effort.

## VIII. ECOLOGICAL CHEMISTRY

The problems of chemical ecology were created by man himself as a result of the continuous (and, during the past century, almost explosive) growth in the industrial activity of mankind. Hence, these problems are artificial to a great extent. However, it would be naive to assume that they can be solved merely by eliminating all sources of ecological pollution, by creating effluent-free (closed) technologies, etc. Some man-made effects in the environment are now too widespread to be reversible, others are slowly reversible, and their elimination would require a great effort and a long time, and a third group of effects are the unavoidable consequences of various technologies (for example, waste products from the nuclear energy industry, contamination from the working of petroleum-bearing underwater shelves, etc.). Hence we need to develop and formulate scientific principles for the elimination, normalisation, and control of harmful or dangerous anthropological effects in the environment, and ecological chemistry should play a major role in this work.

Man-made effects are most marked in the atmosphere, stratosphere, and hydrosphere. Sources of chemical pollution of the atmosphere include the emission of the oxides of nitrogen, sulphur, and carbon, of aromatic hydrocarbons, olefins, and saturated hydrocarbons. The main problem in atmospheric chemicstry is the analysis of chemical reactions in this multi-component system, the quantitative formulation of their kinetics, and the analysis of oxidation processes by molecular oxygen assisted by photolysis due to sunlight. From such a "catalogue" of atmospheric chemical reactions and their kinetics and energetics we must formulate generalised kinetic models of the chemistry of the atmosphere, including processes such as heat and mass transfer (by diffusion and convection of air masses), the development of temperature gradients, humidity, intensity of the solar radiation, etc. The aim of these models is to identify the most harmful components of atmospheric pollution and to predict their long-term and global consequences. The real (and even pressing) need to solve this problem was underlined by recently discovered effects such as "acid rain", which has caused serious economic and ecological losses in the eastern United States, in Scandinavia, in Europe, and in other regions.

Similar problems are found in the chemistry of the stratosphere. However, they include an additional problem of global importance: the fate of the ozone layer, whose role in determining the life support capability of our planet is well recognised. Concern for the fate of the ozone layer in the stratosphere was first expressed in 1970 in connection with the flight of supersonic aircraft emitting oxides of nitrogen. The latter initiate the decomposition of ozone by the reactions

$$NO+O_3\rightarrow NO_2+O_2$$
$$NO_2+O\rightarrow NO+O_2$$

whose sum produces the overall reaction

$$O_3+O\rightarrow 2O_2$$

with long kinetic chains. Chain generation is by the reaction

$$N_2O+O\rightarrow 2NO$$

and the photolysis of oxygen and ozone provides the source of oxygen atoms.

In addition to supersonic aircraft, the natural life processes of nitrogen fixing bacteria (which are a part of the overall nitrogen fixation cycle) contribute to the emission of $N_2O$. Furthermore, $N_2O$ is a product of the metabolism of nitrogen-containing fertilisers.

It is now clear, however, that the combined threat from all these sources to the ozone layer has been overstated, and that the main threat is from the Freons (especially $CFCl_3$ and $CF_2Cl_2$), now used on a large scale as refrigerants, aerosol

propellants, etc. The photolysis of these compounds produces chlorine atoms which decompose the ozone:

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$

The chlorine atoms catalyse the overall chain process, in which the chain length can reach $10^5$. Chain breaking is produced by the reaction of the chlorine atom with methane, but the concentration of methane in the stratosphere is very low (of the order of 1.5 parts per million).

It has been calculated that if the use of Freons continues at the present level the amount of ozone in the stratosphere could be decreased by 17% by the end of the century (a dangerously high figure). Therefore one of the main problems in ecological chemistry is to produce reliable models of stratospheric chemistry, based on the quantitative kinetics and on the quantum yields of all the elementary thermal and photochemical reactions, allowing for data on the spectroscopy and optics of the atmosphere and of the stratosphere and for recent information on the complex formation of molecular oxygen with fluorine atoms in fluorinated molecules. The latter effect is important because the formation of complexes between Freons and oxygen and their photochemical decomposition could be an effective method of breaking down the Freons in the atmosphere.

The protection of the hydrosphere is an important part of ecological chemistry. The problem includes effluent waters from industrial and agricultural activities and natural effluents containing toxic chemicals, fertilisers, and pesticides leached from the soil. The analysis and control of chemical contaminants and the development of reliable and simple methods of purification have long been recognised as the traditional problems of the ecological chemistry of the hydrosphere.

The contamination of the oceans by petroleum products is another important problem. Petroleum and petroleum chemicals distributed as a thin film on the water surface are oxidised by molecular oxygen (partly by enzyme reactions and partly photochemically) by the well known radical chain mechanism. The resulting products (especially the organic acids) are surface-active substances which cover vast water surfaces and affect the evaporation of the oceans, with serious effects on the biology of the ocean through the dissolution of the oxidation products (many of which are poisonous) and through the alteration of the oxygen balance of the ocean.

The ecological effects of the contamination of the ocean and their long-term consequences have not yet been evaluated: studies of the chemistry of the process, and of their kinetics and thermodynamics, are required in order to establish predictive models.

Chemical and ecological effects in the atmosphere, stratosphere, and hydrosphere can lead to perturbations of the thermal balance and to serious meteorological and climatological consequences. Therefore an overall "chemical" monitoring of the environment is required. It should be organised as a control of the chemical state of the atmosphere, stratosphere, and hydrosphere, aimed at detecting sources of pollution and analysing the evolution of these contaminants under natural conditions. The problem includes the development of methods of chemical analysis with high-level quantitative characteristics (which are also needed in technology and in materials science, see section IX).

Lately, an important topic in ecological chemistry is the evaluation of the chemical effects of socially hazardous undertakings such as the production and testing of substances for chemical warfare and nuclear tests. Their danger and social unacceptability should be obvious not only from social considerations but also from the standpoint of ecological chemistry.

## IX. DIAGNOSTIC AND ANALYTICAL CHEMISTRY

Progress in chemical materials science and in chemical industry would be impossible without a corresponding progress in diagnostic and analytical chemistry. The improvement of existing principles and methods of chemical analysis, and the development of new ones, are important problems in modern chemistry.

It is often said that chemists have received many valuable gifts from physicists: optical and vibrational spectroscopy, X-ray diffraction, neutron and electron diffraction, electronic and nuclear magnetic resonance, etc. This point of view is understandable, but not entirely correct, since the opposite view could be put forward. Undoubtedly, in addition to normal analytical methods (traditional chemical analysis, neutron activation and electrochemical analysis, chromatography, emission spectroscopy, etc.) physical methods are widely used in chemistry for the analysis and characterisation of substances, materials, and processes (X-ray and photoelectron spectroscopy, mass spectrometry, low-energy electron diffraction, Mössbauer spectroscopy, dynamic light and neutron scattering, microwave spectroscopy, etc.). Chemists have made a major contribution to the development of these methods and to the expansion of their metrological and analytical capabilities. Effective advances in analytical and diagnostic chemistry can be expected from the application of general advances in chemistry, physics, and instrument design.

Modern technology requires improved analytical and metrological systems for controlling technological processes, the state of the reactor and of its surroundings, and for detecting the need for corrective action at a usefully early stage thus ensuring stable and reliable process control. This type of system should convert the information on the state of the materials, of the processes, and of the surroundings into signals which can be processed in the normal way, and it should be small, sensitive, and fast acting, so as to respond to rapidly changing conditions.

The sensor detectors are systems of this type: they are cheap and small, fast-responding devices designed to measure the parameters of the surrounding medium and of the technological process (pressure, temperature, chemical composition, etc.), and they have been intensively developed in recent years. They include electrochemical sensors (using solid or traditional electrolytes), piezo-sensors (used for the microweighing of adsorbed gases), sensors based on ion-selective membranes, and others. However, the most sensitive devices are those which use semiconductors as the sensing element. They differ from sensors of other types in being smaller, more reliable, and in responding more rapidly to changes in concentration.

The use of metal-oxide and other semiconductors for determining concentrations in gases relies on the change in impurity conduction of these materials upon the adsorption of certain gases. Adsorption sensors are usually prepared from the semiconducting oxides of various metals (Sn, Zn, Ti, Ni, V, and some others). The initial conductivity of these semiconductors is low, and therefore even the adsorption of a small amount of gas causes a large change in resistance of the detector. The threshold sensitivity of these primary converters is $10^6$–$10^8$ $cm^{-3}$.

The sensors can measure the concentration of different gases: $H_2$, $O_2$, $H_2O$, NO, CO, $CO_2$, $H_2S$, $SO_2$, hydrocarbons, etc. However, their selectivity is low, due to the specific properties of adsorption and diffusion through selective membranes. The extent to which selectivity is a requirement in semiconductor sensors depends on the application envisaged. In many cases a modest selectivity is acceptable (when it is known that only a particular combination of gases can be met

under the experimental conditions). For example, sensors for methane used in coal-mine gas detectors do not need a high selectivity, and their ability to respond to many reducing gases in addition to methane is unimportant.

However, in other situations we need to determine gas concentrations in an atmosphere of unknown composition. In this case the sensor should respond to changes in the concentration of only one component of the atmosphere. A proposed solution of this problem relies on the use of a set of different low-selectivity sensors.

Sensors containing different semiconductors and operating at different temperatures give different responses to the adsorption of different gases. The temperature dependence of the conductivity of a pellet of $SnO_2$ baked at 500 °C and treated in $SO_2$ at 350–500 °C for 15 min during the adsorption of different gases is shown in Fig.8. We conclude from these plots that by an appropriate choice of sensor and of working temperature we can produce a set of detectors which can jointly identify uniquely any composition of the gas mixture to which they are exposed. The signals from the sensors can be converted into a system of equations which are solved by a micro-processor so as to determine the concentration of all the components in any gas mixture. This method of solving the problem of producing a selective detector is more promising and rational than attempting to construct an intrinsically selective sensor, which usually results in a serious loss of sensitivity.

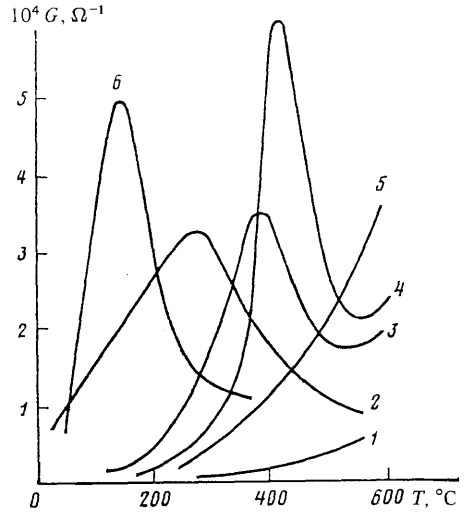



**Figure 8.** Temperature dependence of the sensitivity of a sensor based on $SnO_2$ baked at 500 °C and activated with $SO_2$ (1000 ppm) at 350–500 °C: *1*) air, *2*) $SO_2$, *3*) n-pentane (1000 ppm), *4*) ethylene and butane (0.7%), *5*) methane and ethane (1000 ppm), *6*) hydrogen sulphide (40 ppm).

These sensors have a relatively high sensitivity. A typical threshold sensitivity is 1 ppm (part per million) or less, but for some gases it can be a few ppb (parts per billion). In the detection of active gas particles (atoms, radicals, excited molecules) the sensitivity of semiconductor sensors is even higher (up to $10^{-6}$ mg $cm^{-3}$). It can even exceed the physiological sensitivity of the human nose.

One of the most important characteristics of the sensor is its response time, i.e. its speed of action. Clearly, the shorter the response time, the sooner can an operator monitoring the displayed signal take the required corrective action in response to changes in composition within the reactor or in the surroundings. The response times of the sensors can be long, reaching several minutes in the piezo-detector and in detectors relying on solid electrolytes, but in semiconductor sensors the response time can be ~10 ms.

The main advantage of semiconductors over other types of sensor is their small size and weight. The size of any semiconductor device is determined primarily by the size of the dielectric substrate on which the semiconductor is carried: this is not usually more than a few square millimetres, with a thickness of the order of 1 mm. A whole set of semiconductor detectors can be deposited on a single dielectric substrate to give a multiple assembly weighing only a few grammes.

An important problem in the development of sensor devices is their technological feasibility on a large scale. In recent years micro-electronic and computer technology have reached such a high level that information processing and display systems working in real time can be produced routinely in industry. Semiconductors can therefore be produced in large batches by existing microelectronic technologies.

The development and formulation of new analytical and metrological principles, systems, and devices is another problem in modern chemistry. The range of applications is almost limitless: from the analysis of the chemical composition of substances from the composition of their vapour, even at very low pressures, to the detection of trace impurities and of toxic substances in the atmosphere and to the control of the state of materials, articles, and assemblies. For example, the ageing of concrete produces various gases, varying in amount and composition as the ageing proceeds. A diagnosis of the age of concrete and a prediction of the likely collapse of concrete structures can be based on this effect. This new principle in technological non-destructive testing can be applied to the diagnosis of the state and likely future behaviour of the most diverse materials and structures. Obvious application are in geophysics, vulcanology, gas and petroleum prospecting, and other branches of science and technology.

The principles of analysis with semiconductor detectors can also be applied successfully in medical diagnostics. For example, the composition of gaseous metabolic products in a living organism (evolved in breathing) and the presence of some trace components can be used to diagnose functional anomalies in certain organs and to detect illnesses at an earlier stage than by using conventional methods of diagnosis.

## X. CONCLUSIONS

Chemistry, like any other science, solves or tries to solve a very large number of problems covering a wide range of level and scale, economic importance, and general value, and it is important not to lose sight of the main outlines of chemical science and of their changes with time in the ever-increasing flow of publications.

The aim of the present review was to define the most important and most up-to-date directions in modern chemistry. We tried to assess these directions objectively, and to avoid any bias from our personal scientific interests and commitments. We could be accused of presenting an incomplete or cursory

analysis of the problems, but as any thoughtful reader will understand a fully comprehensive discussion is out of the question in a review of this type.

Every scientific endeavour, every scientific search (including chemical ones) should answer three main questions: what, why, and how. The first question concerns what to seek, what to do, what is the value of the search; the second asks why should the work be done, are the expected results useful, or necessary, where can it be applied, how can it affect various areas of science, technology, and production; the third question asks what is the most rational method of carrying out the work, and how to choose the best, quickest, and most reliable and economical path towards an unambiguous solution of the problem as defined. This logical organisation of scientific research corresponds to that used in the present review: part of the review deals with the questions "what" and "why" (sections V–X), and part with the question "how" (sections II–IV).

We hope to take up the theme of this paper again in a few years, and to assess the extent to which the problems outlined here have been solved and the correctness of the present predictions.

Translated from *Uspekhi Khimii*, **55**, 1979-2007 (1986) U.D.C. 541.49

# Oxallyl Complexes in Organic Synthesis

M.G.Vinogradov, I.P.Kovalev, and G.I.Nikishin

The review is devoted to new methods of synthesis of carbonyl and other oxygen-containing compounds involving oxallyl complexes of transition metals.
The bibliography includes 180 references.

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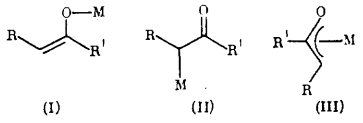
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## I. INTRODUCTION

The allyl compounds of metals constitute one of the most thoroughly investigated classes of organometallic compounds. Numerous reviews and monographs have been devoted to the use of the allyl complexes in synthesis. The metal oxallyl complexes, in which one of the carbon atoms of the allyl system has been replaced by oxygen and which have a similar structure, have been investigated to a much lesser extent. At the same time the continuous growth of interest during the last 5–10 years in the use of oxallyl complexes in organic synthesis and metal complex catalysis makes it essential to survey the scattered literature data available in this field. The present review is the first survey of the employment of oxallyl complexes of transition metals in organic synthesis.

## II. GENERAL CHARACTERISTICS OF OXALLYL COMPLEXES AND METHODS OF THEIR SYNTHESIS

Oxallyl complexes can exist in three forms: (a) as enolates having an oxygen–metal σ-bond (I); (b) as 2-oxoalkyl derivatives of metals having a carbon–metal σ-bond (II); (c) as π-oxallyl complexes (III):



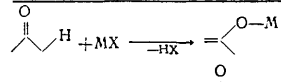
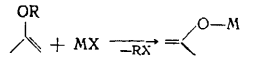
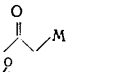
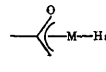
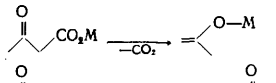
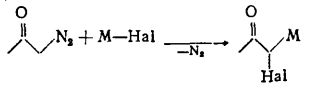
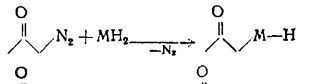
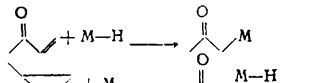
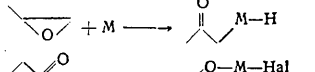
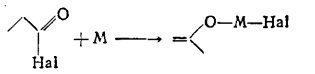
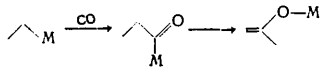
(I) (II) (III)

The existence of oxallyl complexes in a particular form depends on the nature of the metal itself and on the ligands linked to it. In solution there may be equilibrium between the above forms analogous to the equilibrium between the σ- and π-allyl structures of allyl complexes.[1] For example, the transition of the σ-oxallyl complex (II) of iron to the π-oxallyl form (III) under mild conditions has been described.[2] Since many oxallyl complexes are active intermediates in chemical reactions, they cannot be always isolated or identified in solution by spectroscopic methods. In this case their intermediate formation can be inferred from the structure of the reaction products or on the basis of kinetic data.

Metal oxallyl complexes can be obtained (usually *in situ*) by various methods which are summarised in Table 1.

Enol ethers and α-halogeno-, α-diazo, and β-carboxy-substituted and αβ-unsaturated carbonyl compounds are most often used to obtain oxallyl complexes. In addition, they can be obtained from epoxides, acid chlorides, and acyl or

**Table 1.** Methods of synthesis of oxallyl complexes.

| Reaction | Refs. |
|---|---|
|  | M=Fe [9*], Ti [10] |
|  | M=Pd [3*, 4*, 5*], Pt [7, 8*], Au [11] |
|  | M=Pd [6*] |
|  | M=Pd [13], Fe [14*], Cu [14*], Sn [18], Ag [15*], Ti [16*] |
|  | M=Pd [13], Sn [17, 18], Au [19] |
|  | M=Pd [12] |
| R = $SiMe_3$, Ac, All | |
|  | M=Fe [20, 21] |
|  | M=Fe [2] |
|  | M=Cu [22], Pd [23*] |
|  | M=Os [25] |
|  | M=Pd [24] |
|  | M=Os [25] |
|  | M=Fe [26, 27], Os [25], Mo [28, 29], W [29, 30*], Co [31–38] |
|  | M=Ir [39, 40], Rh [80], Pd [40], Pt [40] |
|  | M=Ta [41], Nb [41], Ti [42] |
|  | M=Zr [43, 44, 47, 48], U [45], Th [45], Ta [46] |

*The oxallyl complexes were detected by spectroscopic methods or their intermediate formation has been postulated.

Note. Here and in the other Tables the numerals in square brackets denote references (Ed. of Translation).

alkyl complexes of metals. The references quoted in Table 1 apply mainly to communications in which the isolation of oxallyl complexes has been reported and which contain data on their structure.

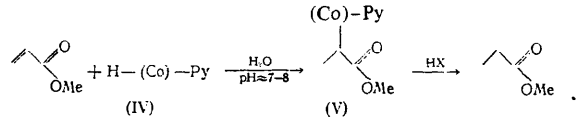
## III. REACTIONS WITH PARTICIPATION OF OXALLYL COMPLEXES

### 1. Reactions Without the Formation of New C–C Bonds

#### (a) Hydrogenation

The hydride and other complexes of molybdenum,[28] iron,[49] cobalt,[32,50,51] ruthenium,[52] rhodium,[53] osmium,[25] and iridium[54] have been used as reagents or catalysts for the reduction of the double bond in αβ-unsaturated carbonyl compounds. As a rule, the reduction takes place under mild conditions (20–65°) at normal hydrogen pressure with a high yield of the saturated carbonyl compound.

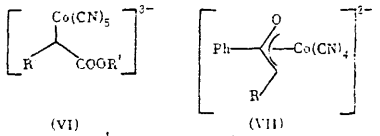
Metal oxallyl complexes are formed as intermediates in the hydrogenation reaction, which has been demonstrated, for example, in the reaction of $Cp_2MOH_2$ with esters of maleic, fumaric, and acrylic acids[28] and also in the reaction of the hydride derivative of cobaloxime (IV) with methyl acrylate:[51]




(IV) (V)

The cobalt complex (V) has been isolated and its thermal stability and chemical properties have been investigated.[51] Metal oxallyl complexes of this type are models of the active intermediates in enzyme reactions with participation of coenzyme $B_{12}$.[35]

In the presence of hydrogen the hydrogenation of αβ-unsaturated carbonyl compounds proceeds as a catalytic reaction. Cobalt carbonyls[55] or $Na_2Co(CN)_5$[31,51,56,57] are more often used as catalysts. The intermediate complexes (VI)[31] and (VII)[51] have been detected spectroscopically in these reactions:

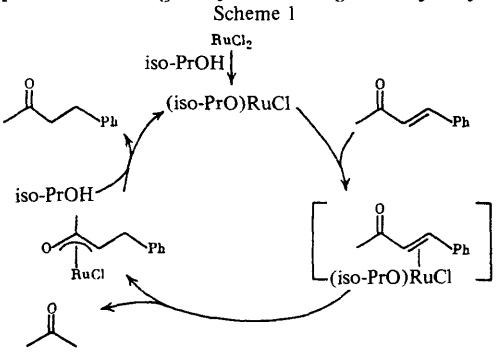



(VI) (VII)
R = H, Me; R' = H, Et R = Me, Et

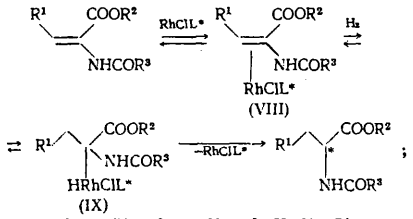
Ruthenium catalysts, for example $RuCl_2(PPh_3)_3$ at 180 °C in a primary or secondary alcohol, have also been used for the catalytic reduction of αβ-unsaturated carbonyl compounds (Scheme 1, the phosphine ligands are not shown). The catalytic yield of the hydrogenation products was $10^4$–$10^5$%.[52]

The reduction of αβ-unsaturated ketones in the presence of the complexes $IrXL_n$ (X = Cl, I, $ClO_4$; L = o-phenanthroline, bipyridyl, or substituted bipyridyls) and KOH in ethanol proceeds analogously with a high catalytic yield.[54]

Scheme 1

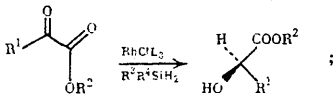



The reduction of prochiral olefins catalysed by rhodium complexes with chiral phosphine ligands takes place stereoselectively and leads to the formation of (*R*)- or (*S*)-substituted α-aminoacid esters with an optical purity of 85–89%.[53,58,59] The intermediate complexes (VIII) and (IX) have been isolated and characterised:[59,59]




R¹=H, Ph; R²=H, Me; R³=H, Me, Ph.

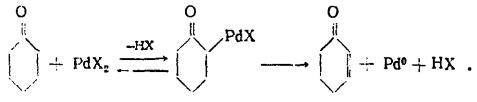
The reduction of α-ketoacids esters by silanes, catalysed by rhodium complexes with chiral ligands, for example, (*R*)-(+)-benzylmethylphenylphosphine, makes it possible to obtain (*R*)-lactates with an optical purity of 30–85%.[60] The mechanism of this reaction is probably similar to that quoted above:




R¹ = Me, Ph; R² = Et, n-Bu, iso-Bu, Ph;
R³ = R⁴ = Me, Et, Ph.

#### (b) Dehydrogenation

With the aid of the metal complexes, it is possible to achieve the αβ-dehydrogenation of carbonyl compounds. Palladium(II) compounds are as a rule used for this purpose: $PdCl_2$,[3,4,12] $PdCl_2(MeCN)_2$,[61] $PdCl_2(PhCN)_2$,[4,5,12] $PdCl_2$·$(PhCN)_2$–AgOTf,[62] $PdCl_2(PPh_3)_2$,[23] $Pd(OAC)_2$,[12,63,64] and $Pd(OAc)_2$–dppe.[65,67]† The dehydrogenation proceeds via a stage involving the formation of oxallyl complexes of palladium(II), which have been in many instances isolated and characterised:[12]

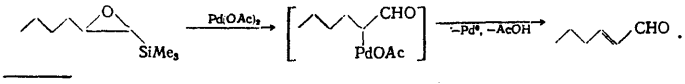



The reactivity of aliphatic and alicyclic ketones in the dehydrogenation reaction catalysed by $PdCl_2(PhCN)_2$ decreases in the sequence cyclohexanone > cyclopentanone > cyclo-octanone > 2-heptanone ≅ 4-heptanone, i.e. cyclic ketones are more reactive than aliphatic ones.[4] Dicyclic ketones are dehydrogenated less effectively than monocyclic ones.

The oxidative decarboxylation of salts of carboxylic β-keto-acids when these interact with $PdCl_2(PPh_3)_2$ also leads to αβ-unsaturated ketones.[23]

αβ-Unsaturated β-aminoketones have been synthesised by dehydrogenating β-aminoketones with the aid of $PdCl_2L_2$ (L = MeCN) in the presence of triethylamine in 50–95% yield.[61]

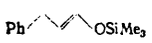
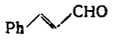
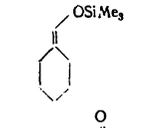
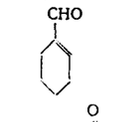
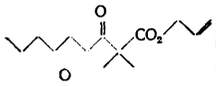
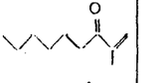
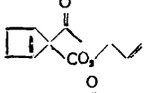
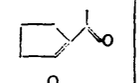
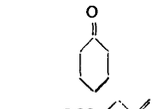
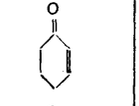
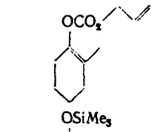
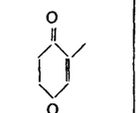
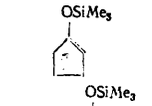
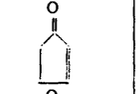
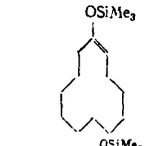
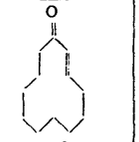
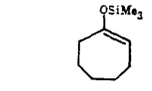
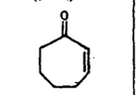
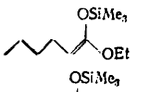
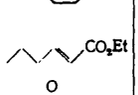
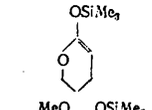
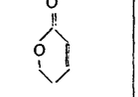
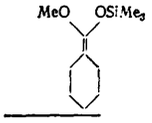
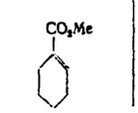
A somewhat unusual method of synthesis of αβ-unsaturated aldehydes and ketones from αβ-epoxysilanes has been proposed:[63]




†Tf = $CF_3SO_2$ and dppe = diphenylphosphinoethane.

Apart from the dehydrogenation of carbonyl compounds and their derivatives by a stoichiometric amount of palladium(II), catalytic versions of this reaction have been developed in recent years (Table 2). The simplest of these is the catalytic dehydrogenation of ketones with the aid of $Pd(OCOCF_3)_2/Cu(OCOCF_3)_2/O_2$ system.[6] The reaction can be carried out catalytically also in the presence of methylallyl carbonate, which behaves as an oxidant in relation to zerovalent palladium (Scheme 2).[67,68] Methylallyl carbonate is consumed in the course of this reaction with formation of $CO_2$ and propene. The silyl ethers of enols are usually employed in this catalytic system.[67]

**Table 2.** Catalytic dehydrogenation of carbonyl compounds and their derivatives in the presence of palladium complexes.*

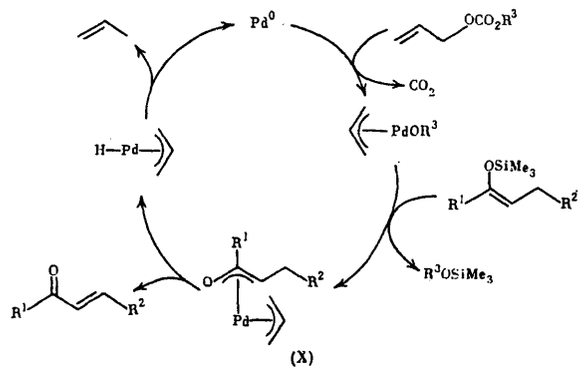
| Initial compound | Catalytic system** | Solvent, temperature, °C | Reaction product | Yield w.r.t. initial compound, % | Refs. |
|---|---|---|---|---|---|
|  | $Pd(OAc)_2$, dppe, AMC | MeCN, 80 |  | 80 | [67] |
|  | » | » |  | 74 | [67] |
|  | $Pd(OAc)_2$, dppe | » |  | 76 | [66] |
|  | » | dioxan, 100 |  | 57 | [66] |
|  | $Pd(OOCCF_3)_2$, $Cu(OOCCF_3)_2$, $O_2$ | —, 20—25 |  | 85 | [6] |
|  | $Pd(OAc)_2$, dppe | MeCN, 80 |  | 98 | [65] |
|  | $Pd(OAc)_2$, dppe, AMC | PhCN, 190 |  | 69 | [67] |
|  | » | MeCN 80 |  | 78 | [67] |
|  | $Pd(OAc)_2$, dppe, AMC, $MeOSnBu_3$ | » |  | 70 | [67] |
|  | $Pd(OAc)_2$, AMC | » |  | 79 | [64] |
|  | » | » |  | 70 | [64] |
|  | » | PhCN, 190 |  | 75 | [64] |

*[substrate]/[Pd] = 10—100.
**AMC = allyl methyl carbonate.

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

The αβ-unsaturated ketones are formed via an analogous mechanism from enol acetates in the presence of methylallyl carbonate[69] and also from allylenol carbonates[67] and the allyl esters of carboxylic β-ketoacids.[66] In all these catalytic reactions the common key intermediates are mixed allyloxallyl complexes of palladium (X) (see Scheme 2).

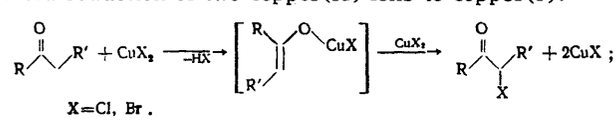
Scheme 2



(X)

(c) Halogenation

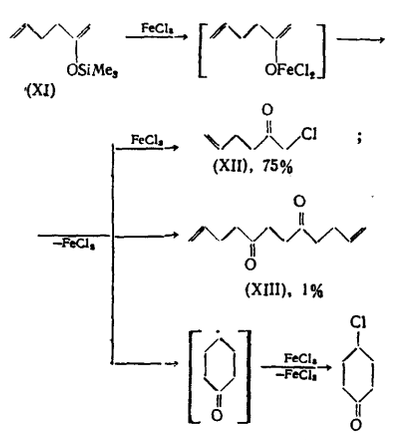
Copper(II) and iron(III) salts are used as a rule for the halogenation of carbonyl compounds (aldehydes, ketones, and esters). The α-halogenocarbonyl compound is formed on halogenation by copper salts probably as a result of the concerted reduction of two copper(II) ions to copper(I):[70]



X=Cl, Br.

The relative reactivity of aliphatic ketones in the reaction with $CuCl_2$ varies in the sequence 2,2-dimethyl-3-pentanone (0.05) < 3-methyl-2-butanone (0.25) < 2-butanone (0.5) ≅ 2-hexanone (0.5) < acetone (1.0). The following sequence has been obtained for cycloalkanones: cyclobutanone (0.01) ≪ cyclopentanone (0.38) < 2-methylcyclohexanone (0.53) < 4-t-butylcyclohexanone (0.94) < cyclohexanone (1.0).[71]

α-Halogenoketones have also been obtained by the interaction of the silyl ethers of enols with $CuCl_2$ or $FeCl_3$ at 20 °C in dimethylformamide (DMF) or MeCN respectively (Table 3). In the presence of $FeCl_3$, the diketone (XIII) and chlorocyclohexanone (XIV) are also formed from the ether (XI) in addition to the main product (XII), which may indicate a cryptoradical mechanism of the chlorination reaction:[14]



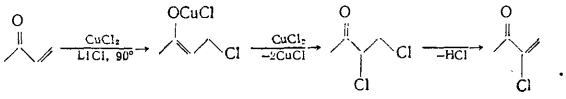
(XI)

(XII), 75%

(XIII), 1%

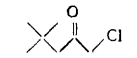
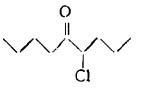
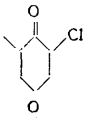
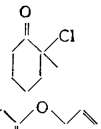
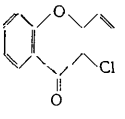
(XIV), 24%

The halogenation of αβ-unsaturated carbonyl compounds also proceeds with retention of the double bond in accordance with the following postulated scheme:[70]



The halogenation of acetylenecarboxylic acid esters with copper chloride or bromide leads to esters of αβ-dihalogeno-substituted αβ-unsaturated acids.[72]

Table 3. The synthesis of α-chloroketones from the corresponding silyl ethers.[14]*

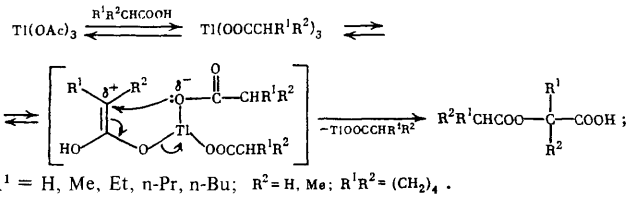
| Metal chloride | α-Chloroketone | Yield, % |
|---|---|---|
| $CuCl_2$ |  | 65 |
| $CuCl_2$ |  | 70 |
| $CuCl_2$ |  | 58 |
| $CuCl_2$ |  | 58 |
| $FeCl_3$ |  | 76 |
| $CuCl_2$ |  | 61 |

*Solvent—DMF ($CuCl_2$) or MeCN ($FeCl_3$); molar ratio ether/salt = 1:(2–3) for $CuCl_2$ and 1:(4–5) for $FeCl_3$; reaction temperature 20 °C.

(d) Oxidation

The oxidation of carbonyl compounds by metal salts can also proceed via two pathways: with formation of compounds having a functional group in the α-position or oxidative cleavage products.

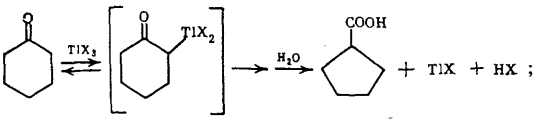
When thallium(III) carboxylates are heated in an excess of carboxylic acid (120–160 °C), α-acetoxyacids are formed[73] in 65–96% yield, thallium(III) being reduced under these conditions to thallium(I). A reaction mechanism involving the formation of an enolate complex has been proposed:



$R^1$ = H, Me, Et, n-Pr, n-Bu; $R^2$ = H, Me; $R^1R^2 = (CH_2)_4$.

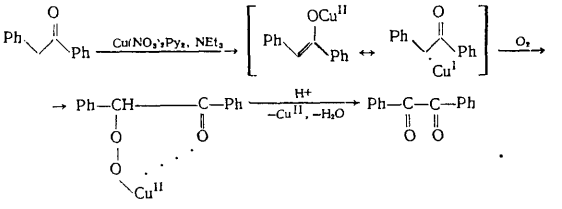
Branched carboxylic acids are oxidised by thallium(III) acetate less effectively than acids having the straight-chain structure. The reactions involving the use of mercury[74] and lead[74] carboxylates proceed analogously.

The oxidation of cyclohexanone by thallium(III) ions leads to the formation of cyclopentanecarboxylic acid:[75]

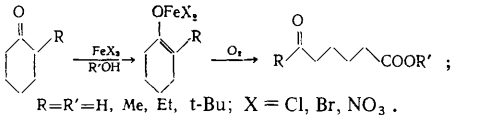


X = OAc.

When certain ketones and esters are oxidised by oxygen in the presence of catalysts (pyridinecopper complexes), α-diketones or α-ketoacid esters are formed in 40–70% yield:[76–78]



The alkyl esters of carboxylic 6-ketoacids have been obtained in 65–95% yield by oxidising 2-alkylcyclohexanones or the acetates of the corresponding enols with oxygen in an alcohol–benzene medium at 60 °C, the reaction being catalysed by iron(III) salts [ketone/Fe(III) = 20–50]. The reaction also probably takes place via the intermediate formation of the oxallyliron(III) complex:[79]

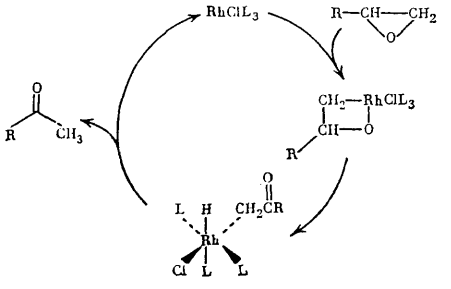


R=R′=H, Me, Et, t-Bu; X = Cl, Br, $NO_3$.

(e) Isomerisation of Epoxides and Other Compounds

1,2-Epoxides are isomerised to carbonyl compounds in the presence of palladium, rhodium, or ruthenium catalysts (Table 4). The mechanism of the isomerisation reaction (Scheme 3) has been investigated in relation to catalysis by rhodium complexes.[80,81] The oxallyl complex (XV; R = Me or Ph; L = $PMe_3$), formed as an intermediate as a result of the oxidative addition of the epoxide to $ClRhL_3$ and subsequent transfer of the β-hydrogen atom, has been isolated and characterised.[80] The rate of isomerisation of *trans*-stilbene oxide to benzyl phenyl ketone, catalysed by the complexes $(p\text{-}XC_6H_4P)_3RhCl$, increases in the following sequence of substituents X: Cl < H < Me < OMe.

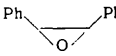
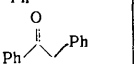
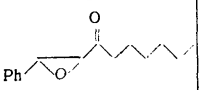
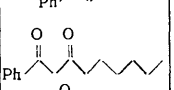
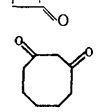
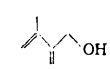
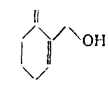
Scheme 3



The phosphine complexes of ruthenium[82] are less effective isomerisation catalysts than the rhodium complexes.

The isomerisation of α-ketoepoxides catalysed by $Pd(PPh_3)_4$ leads to 1,3-diketones,[83] while the isomerisation of the monoepoxides of 1,2-dienes using the same catalysts affords either substituted allyl alcohols or βγ-unsaturated carbonyl compound, depending on the structure of the epoxide.[84]

Table 4. The synthesis of carbonyl compounds and alcohols by the catalytic isomerisation of epoxides.*

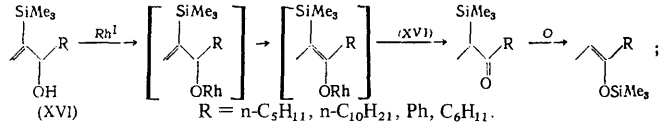
| Epoxide | Catalyst | Solvent, temperature, °C | Product | Yield of product, moles per mole of complex | Refs. |
|---|---|---|---|---|---|
|  | $RhCl(PMe_3)_2$ | —, 70 |  | 85 | [80] |
|  | » | —, 25 |  | 12 | [80] |
|  | $RhCl(PPh_3)_3$ | 1-methylnaphthalene, 210 |  | 43 | [81] |
|  | $Pd(PPh_3)_4$ | toluene, 140 |  | 16 | [83] |
|  | » | toluene, 80 |  | 30 | [83] |
|  | » | toluene, 140 |  | 10,4 | [83] |
|  | » | $Et_2O$, 0 |  | 150 | [84] |
|  | » | benzene, 110 |  | 135 | [84] |
|  | » | $Et_2O$, 60 |  | 800 | [84] |
|  | » | THF, 50 |  | 180 | [84] |

*In the examples quoted, the degree of conversion of the epoxide was ~85–95% and the yield of product with respect to the epoxide which has reacted was ~100%.

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

The isomerisation of phenyl-substituted epoxides in the presence of $Fe(CO)_5$ is a stoichiometric reaction and takes place only under the influence of UV irradiation.[85]

The isomerisation of trimethylsilyl-substituted allyl alcohols (XVI), catalysed by $HRh(CO)(PPh_3)_3$ in the presence of a small amount of α-trimethylsilylketone (1 mole per mole of the complex) at 105 °C in benzene, leads to trimethylsilyl enol ethers:[86]



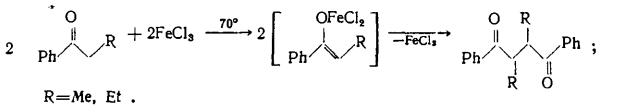
(XVI)

R = n-$C_5H_{11}$, n-$C_{10}H_{21}$, Ph, $C_6H_{11}$.

## 2. Reactions with Formation of New C=C Bonds

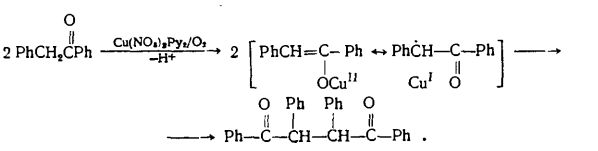
### (a) Dimerisation of Carbonyl Compounds and Their Derivatives

One-electron oxidants, namely iron(III) and copper(II) salts, $TiCl_4$, or $Ag_2O$, are used for the dehydrodimerisation of carbonyl compounds. Thus the dehydrodimerisation of alkyl aryl ketones in the presence of $FeCl_3$ leads to substituted 1,4-diketones in 50–85% yield relative to the oxidant:[87]

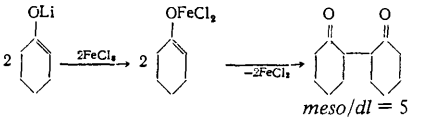


R=Me, Et .

1,4-Diketones are formed analogously from 2-butanone and 2-methyl-4-pentanone, but in a smaller yield (25–35%), when acted upon by the pyridine complex of copper(II) in the presence of $PPh_3$ in methanol at 40 °C.[77] The dehydrodimerisation of deoxybenzoin in the presence of pyridine-copper complex and oxygen proceeds as a catalytic reaction:[76]



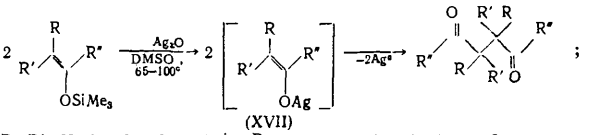
Lithium enolates[88,90] and silyl ethers of enols[91] have also been used as the starting compounds for the synthesis of 1,4-diketones. For example, the oxidative dimerisation of the lithium enolate derived from cyclohexanone, catalysed by $FeCl_3$, leads to a mixture of diastereoisomeric diketones with the *meso*-isomer predominating:[88]



*meso*/*dl* = 5

The yield of the 1,4-diketone obtained from the lithium t-butyl methyl ketone enolate is also influenced by the nature of the anion in the copper salt:[89] $CuCl_2$ (92) > $CuBr_2$ (64) > $Cu(acac)_2$ (60) > $Cu(OAc)_2$ (24).

It is believed that the reaction of silyl ethers of enols with $Ag_2O$ proceeds with the intermediate formation of the silver enolate (XVII):[15]



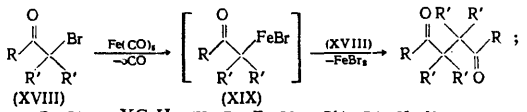
(XVII)

R=R′=H, Me; R″=Me, Et, iso-Pr, Ph; R, R′=$(-CH_2-)_n$; n=3, 10 .

The yield of the 1,4-diketone (mixture of *meso*- and *dl*-diastereoisomers) is 40–80% and diminishes with increase of the number and bulk of the substituents at the double bond of the silyl enol ether.

The mechanism of the reaction of the enolate (XVII) has not been considered, but it has been shown[92] that $n\text{-}C_4H_9Ag(PPh_3)$ decomposes with formation of n-octane probably via a homolytic mechanism in the coordination sphere of silver ions (via an intermediate dinuclear complex).

1,4-Diketones can be obtained by the reductive dimerisation of α-halogenoketones. When α-bromoketones (XVIII) were allowed to interact with $Fe(CO)_5$ in dimethoxyethane at 95–100 °C, 1,4-diketones were synthesised in 30–65% yield, depending on the structure of the substituents:[2]

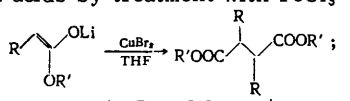


(XVIII) (XIX)

R=Ph, $p$-$XC_6H_4$ (X=Br, F, OMe, Ph); R′=H, Me.

The intermediate oxallyl iron complex (XIX, $R = p$-$PhC_6H_4$, $R' = H$) has been isolated and characterised.

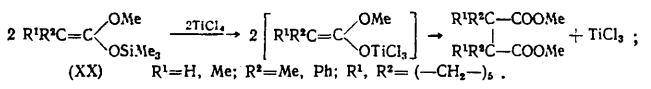
The esters of substituted succinic acids have been obtained in 50–85% yield from the lithium enolates derived from carboxylic acids by treatment with $FeCl_3$ [88] and $CuBr_2$: [93]



R=H, Me, Ph, iso-Pr, n-$C_5H_{11}$; R′ = Et, t-Bu.

The mechanism of this reaction is apparently analogous to that of the dimerisation of ketones and their derivatives.

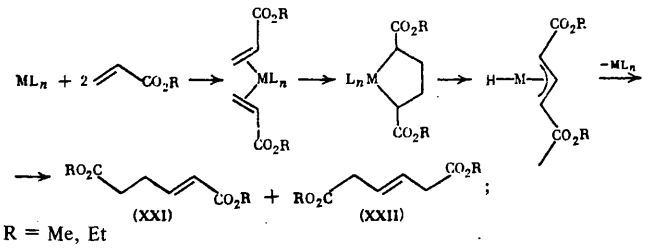
Carboxylic acid derivatives, namely the silyl esters (XX), are also converted into dimeric products—substituted succinic esters (mixture of *meso*- and *dl*-diastereoisomers)—on interaction with $TiCl_4$. The yield is 75–80%.[16] These esters are obtained in a low yield in reactions with copper(II) and iron(III) halides:[16]



(XX) R¹=H, Me; R²=Me, Ph; R¹, R²=(—$CH_2$—)$_5$.

The "tail to tail" dimerisation of αβ-unsaturated carbonyl compounds is catalysed by palladium and rhodium complexes.[94,95] The main product of the dimerisation of methyl acrylate in the presence of $[(C_2H_4)_2RhCl]_2$ or $PdCl_2(PhCN)_2$ catalysts and Lewis acids ($FeCl_3$, $AgBF_4$, and $AgPF_6$) is the unsaturated ester (XXI) containing 90% of the *trans*-isomer [(XXI)/(XXII) = 9] (Scheme 5).

Scheme 5

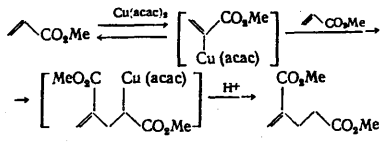


R = Me, Et

The number of catalytic cycles in the presence of the rhodium catalyst at 75 °C reaches 280.

Copper(II) acetylacetonate and CuO catalyse the "head to tail" dimerisation of methyl acrylate in the presence of t-butyl isocyanide in t-butyl alcohol (olefin/Cu = 50). The catalytic yield of the dimerisation product is 50–550% (Scheme 6).[96]

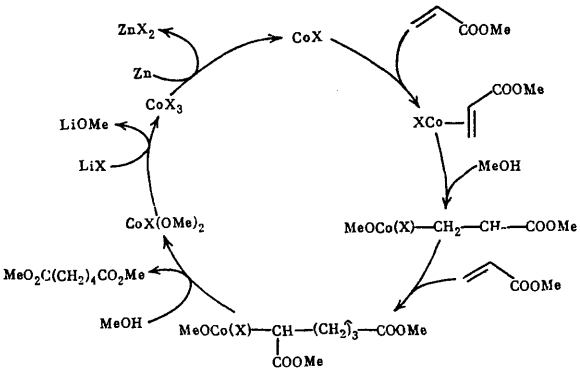
Scheme 6



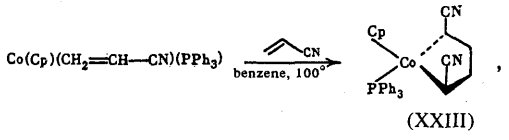
Saturated "tail to tail" dimers have been obtained (2–11 moles per mole of the catalyst) by the hydrodimerisation of methyl vinyl ketone and acrylate esters in methanol on treatment with metallic zinc in the presence of $[Co(bipy)_3]ClO_4$ or $CoBr(PPh_3)_3$.[97,98] The hydrodimerisation of methyl acrylate catalysed by cobalt complexes leads to the dimethyl ester of adipic acid in 25–90% yield relative to the initial acrylate and 50–700% yield relative to the catalyst,[99] the yield of the ester depending on the nature of the anion in the complex $CoX(PPh_3)_3$ and increasing in the following sequence of substituents X: Cl < Br < I.

The proposed reaction mechanism is presented in Scheme 7.[99]

Scheme 7



In the given instance one probably cannot rule out also a mechanism similar to that discussed above for the dimerisation of acrylates in the presence of palladium and rhodium catalysts (see Scheme 5).[95] This is indicated, in particular, by the fact that the intermediate complex (XXIII) (in the form of two geometrical isomers) was isolated in the presence of cobalt catalysts:[100]

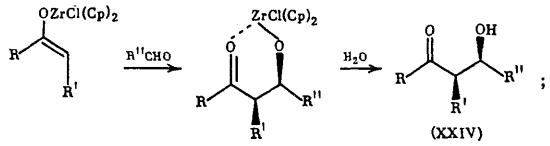


(XXIII)

(b) The Aldol and Crotonic Condensations and Similar Reactions

The use of transition metal complexes makes it possible to achieve the stereo-selective synthesis of aldols from carbonyl compounds and their derivatives.

The zirconium enolates derived from ketones and acid esters and amides, obtained from $ZrCl_2(Cp)_2$ and the corresponding lithium enolates, react with aliphatic and aromatic aldehydes at −78 °C in tetrahydrofuran (THF)[101,102] with formation of more than 90% of the *erythro*-aldol (XXIV):



(XXIV)

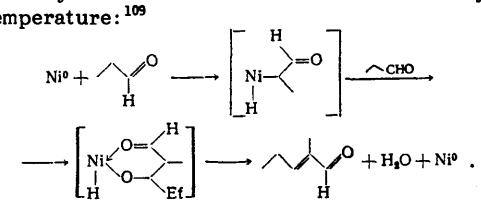
R = OMe, O-t-Bu, S-t-Bu, $N(CH_2)_4$, N(iso-Pr)$_2$, Et,
R′ = Me; R, R′ = (-$CH_2$-)$_3$, (-$CH_2$-)$_4$; R″ = n-Pr, n-Bu, Ph.

The greatest stereoselectivity (95–99%) has been observed for the reaction of zirconium enolates obtained from acid amides with aldehydes having nitrogen-containing heterocyclic substituents.[103] The hydrolysis of the amides yielded the corresponding carboxylic *erythro*-β-hydroxy acids.

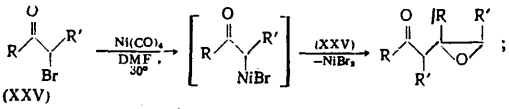
Titanium(IV),[42,104] mercury,[105] and tin[106] enolates react analogously in the presence of $BF_3.OEt_2$ with aliphatic and aromatic aldehydes, forming 70–90% of the *erythro*-aldol. The reaction can also be carried out catalytically using the silyl ethers of enols, for example, when the latter interact with α-alkoxyaldehydes in the presence of $TiCl_4$.[107] The

reaction of silyl ethers of enols with optically active α-keto-acid esters in the presence of $TiCl_4$ leads to the formation of aldols with two optically active centres.[108] The extent of the asymmetric induction (35–70%) is in this case much higher than in the case where organomagnesium compounds are employed.

Complexes of zerovalent nickel, for example (bipy)Ni.$(PPh_3)_2$, catalyse the crotonic condensation of aldehydes at room temperature:[109]



The aldol condensation of α-bromoketones in the presence of $Ni(CO)_4$ leads to substituted βγ-epoxyketones in 50–85% yield:[110]



(XXV)

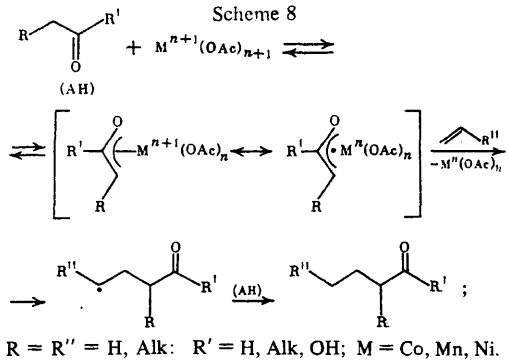
R = Me, Et, t-Bu; R′ = H, Me.

This is the simplest and most effective of the existing methods of synthesis of βγ-epoxyketones.

(c) Alkylation of Carbonyl Compounds

The α-alkylation of aldehydes, ketones, and carboxylic acids by olefins has been achieved on treatment with $Mn(OAc)_3$[111,112] or the redox systems $Mn(OAc)_2/O_2$[113] and $Co(OAc)_2/O_2$[113] (Table 5). The study of the characteristics and kinetics of the alkylation of aldehydes led to a catalytic mechanism of the reaction involving the intermediate formation of oxallyl complexes in which the oxallyl ligand has a radical character (scheme 8):[114]

Scheme 8

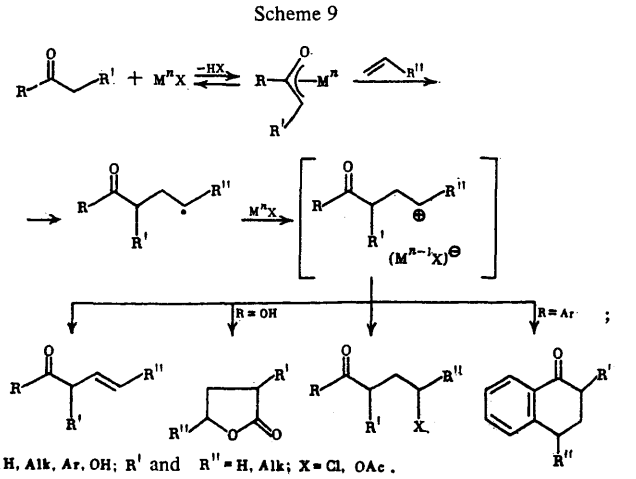


R = R″ = H, Alk: R′ = H, Alk, OH; M = Co, Mn, Ni.

In terms of their selectivity in the α-alkylation reaction, the catalysts can be arranged in the following sequence:[113] Co(II) > Mn(II) ≅ Ni(II) > Ce(III) > Cr(III).

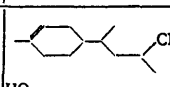
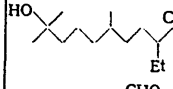
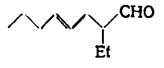
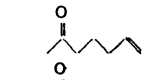
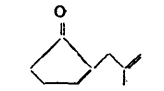
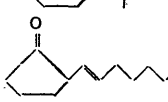
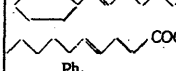
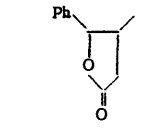
The reaction involving the homolytic *oxidative addition* of aldehydes, ketones, and carboxylic acids to multiple bonds is important for synthetic purposes. Its difference from the alkylation reaction considered above consists in the oxidation of the intermediate adduct-radical to a carbonium ion intermediate. Depending on its structure and the reaction conditions, the latter is capable of reacting via different pathways, for example, β-elimination with formation of an ethylenic bond, of cyclising to a substituted lactone,[118–121] tetralone, and similar compounds,[122] or of interacting with external nucleophiles to form products substituted by functional groups in the γ-position[111,115,119,123] (Scheme 9):

Scheme 9



R = H, Alk, Ar, OH; R′ and R″ = H, Alk; X = Cl, OAc.

Table 5. The synthesis of α-alkyl-substituted carbonyl compounds.

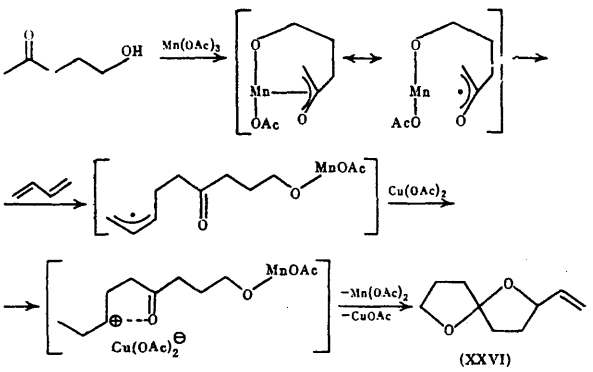
| Carbonyl compound | Unsaturated compound | Initiating system* | t, °C | α-Alkylation product | Yield % | Refs. |
|---|---|---|---|---|---|---|
| EtCHO | dipentene | $Co(II)/O_2$ | 50 |  | 67 | [113] |
| PrCHO | 7-hydroxy-3,7-dimethyl-oct-1-ene | » | 70 |  | 53 | [113] |
| PrCHO | hex-1-ene | Mn(III)/Cu(II) | 60 |  | 40 | [111] |
| Acetone | ethylene | » | 80–100 |  | 70 | [115] |
| Cyclo-pentanone | isobutene | » | 40 |  | 70 | [112] |
| » | hept-1-yne | Mn(III) | 80 |  | 52 | [112] |
| AcOH | oct-1-ene | Mn(III)/Cu(II) | 120 |  | 63 | [116] |
| » | *trans*-β-methyl-styrene | Mn(III) | 135 |  | 79 | [117] |

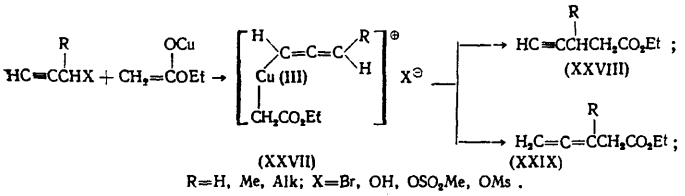
*Metal acetates were used.

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

Other pathways are also possible in this reaction. Thus the vinyl-substituted spiroketal (XXVI)—the direct precursor of chalcogran, which is a pheromone of the conifer bark beetle,[124] has been obtained by the reaction of acetylpropyl alcohol with butadiene catalysed by the $Mn(OAc)_3/Cu.(OAc)_2$ system (Scheme 10). Vinyl-substituted 2,8-dioxa-*cis*-bicyclo[3.3.0]octane is formed together with the spiroketal (XXVI) in this reaction.[124] The reaction of acetone with butadiene proceeds analogously:[124]

Scheme 10





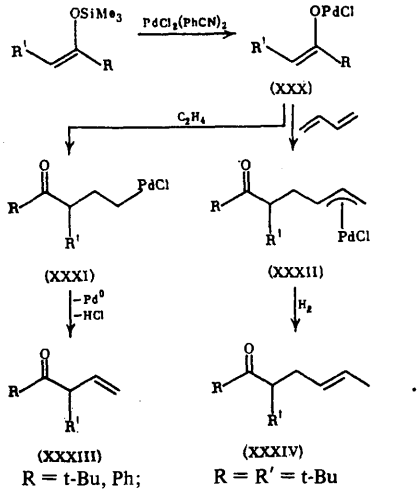
(XXVII) (XXIX)

R=H, Me, Alk; X=Br, OH, $OSO_2Me$, OMs .

The reactions of the oxallyl complexes of copper(I), obtained from the corresponding lithium enolates, with propargyl alcohol and its derivatives result in the formation of the substituted allenes (XXIX) in 45–70% yield. The acetylenic compound (XXVIII) is formed as a side product in this reaction with the ratio (XXIX)/(XXVIII) = 10–20 : 1. The use of lithium enolate in the above reaction leads to only the acetylenic compound (XXVIII). The authors explain the difference by the fact that, in the case where copper enolates are used, the unstable complex (XXVII) is formed as an intermediate.[125]

Palladium(II) complexes have been used in another group of reactions of carbonyl compounds with olefins and dienes. In the presence of $PdCl_2(PhCN)_2$, the silyl ethers of enols react with ethylene and butadiene.[13] The reaction proceeds via the intermediate formation of the palladium enolate (XXX). The complexes (XXX) are isolated in a dimeric form. The reaction of the complex (XXX) with ethylene at 50 °C and a pressure of 50 atm leads to the βγ-unsaturated ketone (XXIII) in 60–75% yield, while the reaction with butadiene leads to the allyl complex (XXXII), whose reduction with hydrogen afforded the γδ-unsaturated ketone (XXXIV) in 65-90% yield (Scheme 11):

Scheme 11



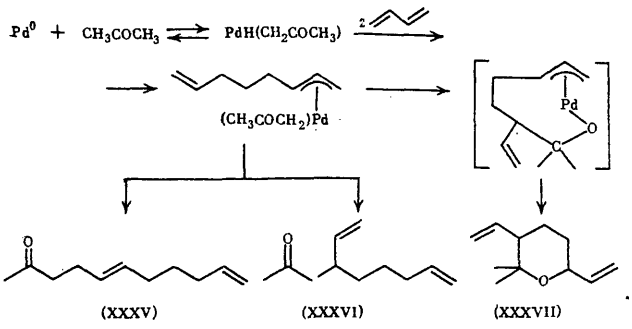
(XXXIII) (XXXIV)

R = t-Bu, Ph; R′ = t-Bu

R = R′ = t-Bu

Palladium complexes, for example $Pd(PEt_3)_4$, also catalyse the addition of two butadiene molecules to acetone[126] (Scheme 12).

Scheme 12



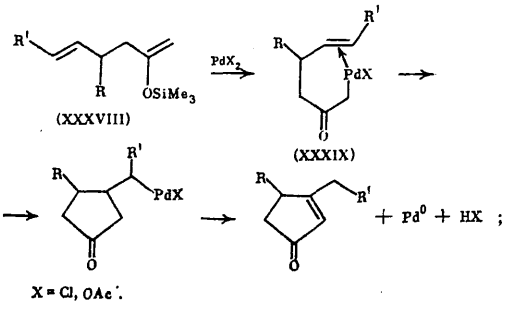
(XXXV) (XXXVI) (XXXVII)

The reaction results in the formation of the isomeric unsaturated ketones (XXXV) (*trans* : *cis* = 10) and (XXXVI) in proportions of 10 : 1 in 11% yield and also 2,2-dimethyl-3,6-divinyltetrahydropyran (XXXVII) (*cis* : *trans* = 3) in 20% yield. The comparatively low yields of the products (XXXV)–(XXXVII) are associated with the side reaction involving the catalytic dimerisation of butadiene to octa-1,3,7-triene. When the trimethylphosphine ligand is replaced by the triphenylphosphine ligand in the initial palladium complex, only the dimerisation of butadiene takes place.

The reaction of cycloalkanones with butadiene in the presence of a palladium catalyst[127] leads to 2-alkadienylcycloalkanones, whose structure is analogous to that of the ketones (XXXV) and (XXXVI) (the ketone with the unbranched substituent predominates). In terms of their reactivity, the cycloalkanones can be arranged in the following sequence: $C_5 > C_8 \cong C_6 > C_7$. The yield of the addition products is 5–30% relative to the initial compound and (3–25) × $10^3$% relative to the catalyst.

The αβ-unsaturated cycloalkanones have been obtained by cyclising the unsaturated silyl enol ethers (XXXVIII) in the presence of palladium(II) compounds[128,129] (Scheme 12a).

Scheme 12a



X = Cl, OAc .

The intermediate oxallyl complexes (XXXIX, R = Ph, R′ = H; RR′ = $(-CH_2-)_{3-5}$] have a dimeric structure. They have been isolated and characterised by physicochemical methods.[129]

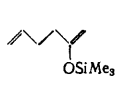
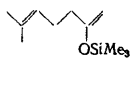
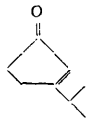
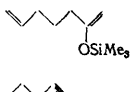
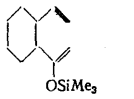
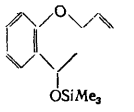
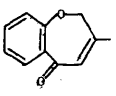
Table 6 presents the known examples of the cyclisation of unsaturated silyl enol ethers catalysed by $Pd(OAc)_2$ in acetonitrile.

(d) Arylation of Carbonyl Compounds

The reactions of acetone with aromatic and heteroaromatic compounds catalysed by $Mn(OAc)_3$ make it possible to introduce the acetonyl group into the aromatic ring under comparatively mild conditions (50–80 °C).[130,131] The reactions

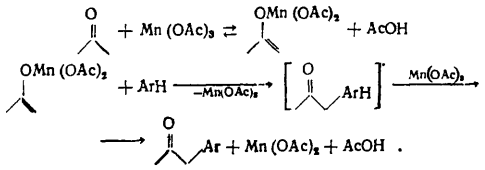
with naphthalene, furan, and thiophen proceed exclusively at the α-carbon atom of the aromatic ring. The yield of 3-aryl-2-propanones is 40–95% with respect to the oxidant.

Table 6. The synthesis of αβ-unsaturated cyclic ketones.[129]*

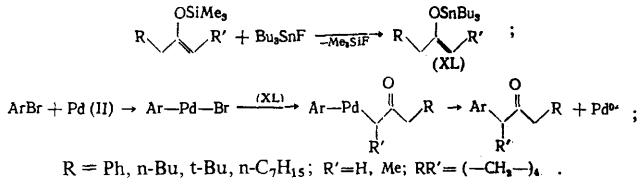
| Silyl enol ether | Ketone | Yield, % |
|---|---|---|
|  |  | 87 |
|  |  | 40** |
|  |  | 36 |
|  |  | 99 |
|  |  | 25 |

*$Pd(OAc)_2$/(silyl enol ether) = 1:1, MeCN, 20 °C.
**Oxidant—$PdCl_2(PhCN)_2$.

In monosubstituted benzenes substitution takes place predominantly in the *ortho*-position in the benzene ring, electron-donating substituents in the ring facilitating the reaction.[131] The reactivities of aromatic compounds in the reactions with acetone decrease in the following sequence: sylvan [α-methyfuran] > furan ≅ naphthalene > thiophen > anisole > benzene ≅ chlorobenzene > benzonitrile.[132] The following reaction mechanism has been proposed:

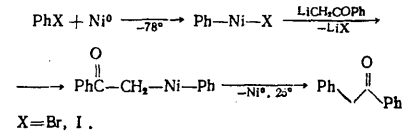


The α-arylation of aliphatic and cyclic ketones is achieved by the interaction of trimethylsilyl ethers of enols or enol acetates with ArBr (Ar = Ph or substituted phenyl) in the presence of $Bu_3SnF$ [133] or $Bu_3SnOMe$ [134] and $PdCl_2[P(o\text{-}MeC_6H_4)_3]_2$ (ArBr/Pd = 30–100) as the catalyst at 80–100 °C in benzene or toluene. The yield of α-aryl-substituted ketones is 30–100%:



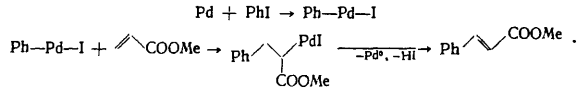
R = Ph, n-Bu, t-Bu, $n\text{-}C_7H_{15}$; R′=H, Me; RR′ = $(-CH_2-)_4$.

α-Aryl-substituted carbonyl compounds have also been obtained by the reaction of phenyl halides with $LiCH_2COPh$ in the presence of $Ni(PPh_3)_4$ [PhX/Ni(0) = 4].[135] The mechanism of this reaction is similar to that quoted above:



X=Br, I.

β-Aryl substituted carbonyl compounds can be obtained by the reaction of aryl halides with αβ-unsaturated carbonyl compounds. Thus the reaction of iodobenzene with methyl acrylate (PhI/Pd = 30), catalysed by metallic palladium (palladium black), at 125 °C in acetic acid in the presence of sodium acetate leads to the formation of methyl cinnamate in accordance with the following suggested mechanism:[136]



When $Pd(PPh_3)_4$ is used as the catalyst, bromobenzene and substituted aryl bromide also enter into this reaction.[137]

The reactions of benzene with α-substituted chalcones in the presence of $Pd(OAc)_2$ (chalcone/Pd = 1–15) in acetic acid lead to saturated or unsaturated ββ-diphenyl-substituted ketones, depending on the structure of the chalcones[138] (Table 7):

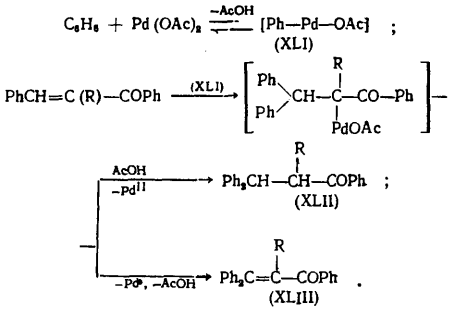


Table 7. The yields (%) of the products of the reactions of benzene with chalcones in the presence of $Pd(OAc)_2$*[138]

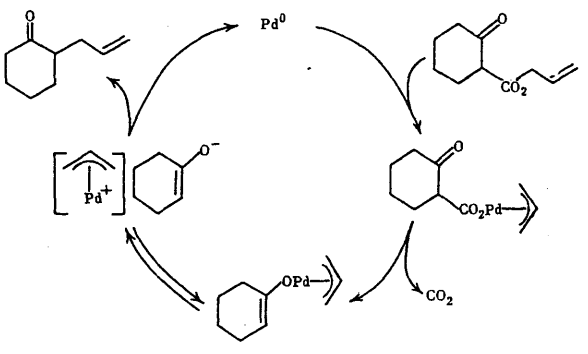
| Product | R | | | | | |
|---|---|---|---|---|---|---|
| | H | Ph | COPh | $NO_2$ | $CO_2Et$ | $CH_2Ph$ |
| (XLII) | 25 | — | 52 | 20 | 12 | — |
| (XLIII) | 75 | 46 | 8 | — | 56 | 66 |

*[chalcone]/[Pd] = 1:1.

(e) α-Allylation of Carbonyl Compounds

A convenient method for the introduction of alkenyl groups into the α-position in carbonyl compounds is based on the use of mixed allyloxallyl complexes of palladium(II) (XLIV) which are formed, for example, from allyl β-ketocarboxylates (Scheme 13).[23]

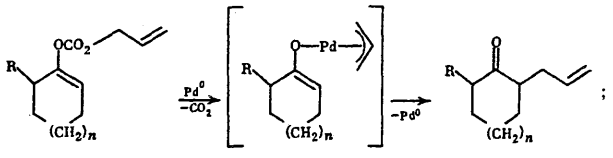
Scheme 13



(XLIV)

In the presence of $Pd(PPh_3)_4$ (ester/Pd = 20), α-allyl-substituted alkanones and cycloalkanones were obtained at room temperature in 60–95% yield.

α-Allyl-substituted carbonyl compounds are also synthesised from allyl carbonates at 0 °C in dimethoxyethane:[139]

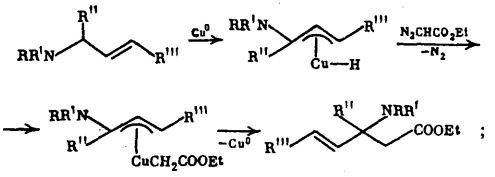


R = H, Me; $n = 0, 1$.

The complexes $Ni[P(OEt)_3]_4$, $RhH(PPh_3)_4$, and $Mo(CO)_6$ can be used as catalysts of this reaction in addition to $Pd(PPh_3)_4$.[140] However, more severe conditions are required (60–110 °C).

Apart from the two reactions examined above, the syntheses of α-allylalkanones and α-allylcycloalkanones by the reaction of silyl enol ethers[64,141] or enol acetates[142] with allyl methyl carbonate in the presence of $Pd(dppe)_2$ and also by the reaction of allyl acetates with tributyltin enolate in the presence of $Pd(PPh_3)_4$ [143] at 20–80 °C in dioxan or THF have been described.

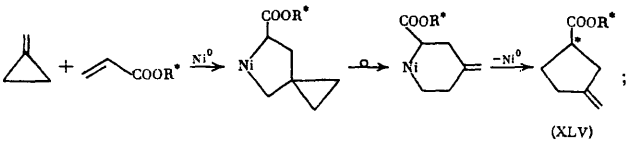
The reactions of ethyl diazoacetate with allylamines (allylamine/metal = 40), catalysed by the $Cu(acac)_2/AlEt_3$ and $Rh_2(OAc)_4/AlEt_3$ systems in the presence of $PEt_3$, $PBu_3$, or pyridine in benzene at 20 °C, lead to esters of β-amino-β-vinyl-substituted carboxylic acids in 20–60% yield.[144] The reaction probably proceeds via the following mechanism:



$RR' = (-CH_2-)_5$, $(-CH_2-)_2-O-(-CH_2-)_2$;
R'' = H, Me; R''' = H, Me, $C_5H_9$.

(f) Cycloaddition to αβ-Unsaturated Carbonyl Compounds

Zerovalent nickel complexes catalyse the cycloaddition of strained molecules, for example, methylenecyclopropane and its derivatives [initial compound/Ni(0) = 30] to αβ-unsaturated ketones and acrylates with formation of substituted methylene-cyclopentanes in 60–90% yield.[145] The reaction is stereoselective. Thus esters of 3-methylenecyclopentanecarboxylic acid (XLV) having two chiral centres have been obtained from methylenecyclopropane and optically active acrylate esters in the presence of Ni(cyclo-octadiene)$_2$ (ester/Ni = 100) at −20–+40 °C. The degree of the asymmetric induction for the second chiral centre is 25–65%.[146]

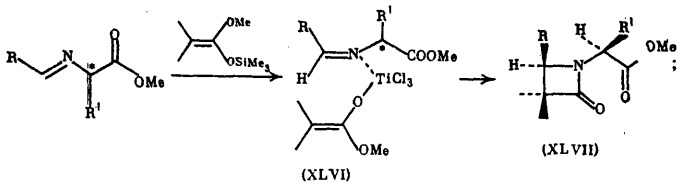


(XLV)

R* = (−)-bornyl, (−)-menthyl, (−)-8-phenylmenthyl.

The cycloaddition of bicyclo[2.1.0]pentane in methyl acrylate, dimethyl maleate, and dimethyl fumarate, catalysed by $Ni(CH_2{=}CHCN)_2$, probably proceeds via a similar mechanism.[147,148]

The reaction of the *O*-trimethylsilyl derivatives obtained from methyl isobutyrate with the Schiff bases obtained from aldehydes and chiral α-aminoethers in the presence of $TiCl_4$ leads to the formation of β-lactams with high regio- and stereo-selectivities.[149,150] Its mechanism involves the formation of the titanium(IV) enolate (XLVI) (detected by spectroscopic methods), which undergoes intramolecular cyclisation with formation of the β-lactam (XLVII), having the (*S*,*R*)-configuration to the extent of 60–99%:

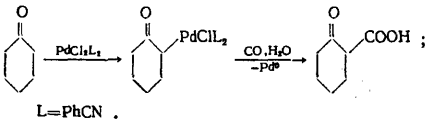


(XLVI) (XLVII)

R = Et, iso-Pr, iso-Bu; R′ = Me, iso-Pr, $CH_2Ph$, $CH_2COOMe$.

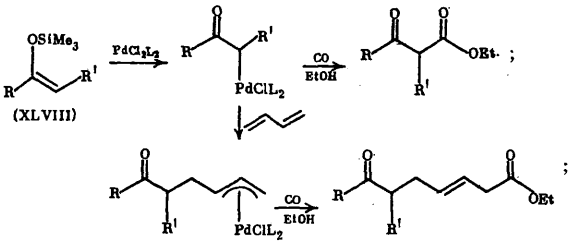
(g) Reactions with Participation of Carbon Monoxide

When the oxallyl complexes of palladium are acted upon by carbon monoxide, carboxylic β-ketoacids are formed in 40–75% yield:[4]



L=PhCN.

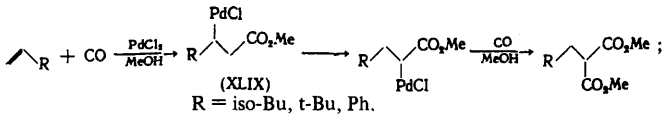
The esters of carboxylic β-ketoacids have been synthesised in 85–100% yield by carbonylating in an alcoholic medium the palladium complexes obtained from silyl enol ethers (XLVIII) (50 °C, 50 atm CO pressure); in the presence of butadiene, the above reaction leads to esters of unsaturated ketoacids:[13]



(XLVIII)

L = PhCN; R = t-Bu, Ph; R′ = t-Bu.

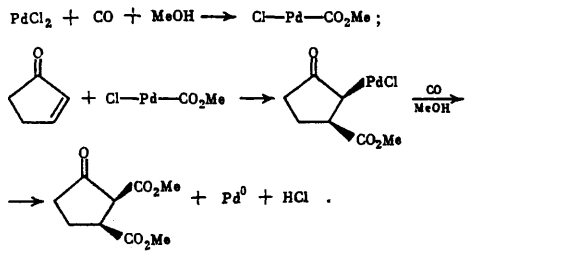
The esters of alkylmalonic acids can be obtained by the carbonylation of alkenes, catalysed by $PdCl_2$, in the presence of an excess of $CuCl_2$,[151] probably via a medium involving the rearrangement of the organopalladium intermediate (XLIX):



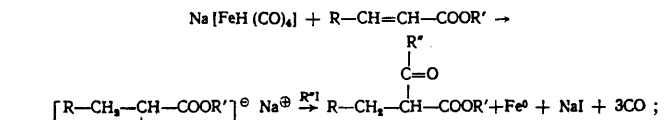
(XLIX)

R = iso-Bu, t-Bu, Ph.

The carbonylation of αβ-unsaturated ketones, catalysed by the $PdCl_2/CuCl_2$ system (ketone/Pd = 10–50, 20 °C, 3 atm CO pressure), leads to esters of substituted succinic acids.[152] The reaction with cyclopentenone results in the 99% yield of the ester of *cis*-3-oxocyclopentane-1,2-dicarboxylic acid:



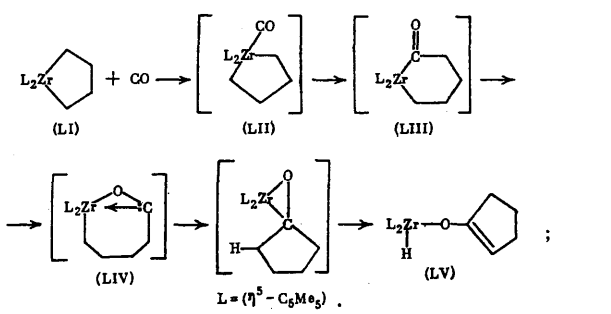
The hydroacylation of esters of αβ-unsaturated carboxylic acids takes place in THF at 20–50 °C with participation of $Na[FeH(CO)_4]$ (stoichiometric amount) and allyl iodide; the yield of β-ketoacid esters is 50–80%.[153] The intermediate oxallyl complex (L, R = H, R′ = Me) was isolated and characterised:



(L)

R=H, Me; R′=R″=Me, Et .

The carbonylation of alkylzirconium complexes leads to the formation of derivatives of carbonyl compounds in high yields (80–95%).[43,154,155] Thus the zirconium complex (LI) readily combines with CO at 25 °C to form the white crystalline enolate (LV), which is quantitatively converted into cyclopentanone on treatment with HCl.[43] The reaction probably proceeds via the successive formation of the carbonyl intermediates (LII), the acyl intermediate (LIII), and the carbenoid intermediates (LIV):

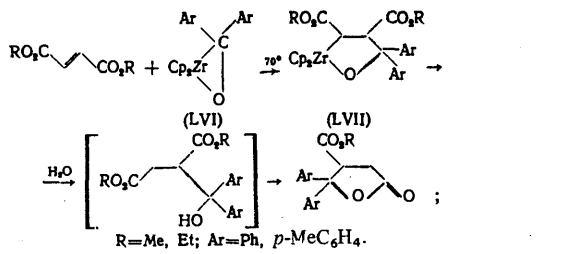


(LI) (LII) (LIII) (LIV) (LV)

L = ($\eta^5$-$C_5Me_5$) .

(h) Other Reactions

γγ-Diarylbutyrolactones have been synthesised in 80–85% yield by the reaction of maleate and fumarate esters with organozirconium compounds (LVI):

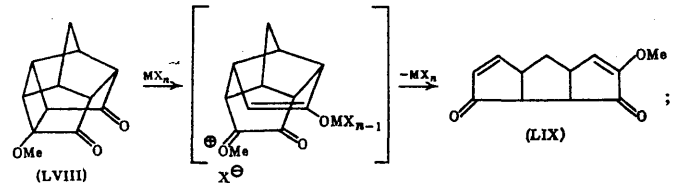


(LVI) (LVII)

R=Me, Et; Ar=Ph, *p*-$MeC_6H_4$.

The intermediate oxallyl complexes (LVII) have been detected by $^1H$ NMR.

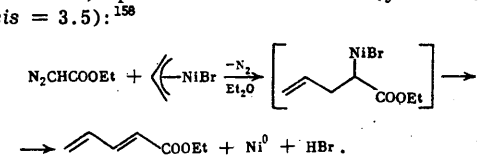
The unsaturated diketone (LIX) has been obtained in 65–70% yield as a result of the catalytic decyclisation of the polycyclic ketone (LVIII) at 40 °C in benzene or $CHCl_3$ (ketone/$MX_n$ = 10):[157]



(LVIII) (LIX)

$MX_n = TiCl_4, PdCl_2$ .

The reaction of ethyl diazoacetate with (π-allyl)NiBr at 0 °C leads to 2,4-pentadienoic acid ester (yield 90%, *trans*/*cis* = 3.5):[158]



Thus examination of the data presented shows that the oxallyl complexes of transition metals plays an important role in the reactions of carbonyl compounds and their derivatives such as hydrogenation, oxidation, halogenation, dimerisation, alkylation, etc. Many of these reactions are catalytic and involve the formation and further reaction of oxallyl intermediates. The use of oxallylmetal complexes in stoichiometric and catalytic reactions makes it possible to synthesise various carbonyl compounds under mild conditions with a high regioselectivity and, in a number of instances, also high stereoselectivity.

The chemistry of oxallyl complexes of transition metals constitutes a branch of metal complex catalysis which has been rapidly developing since the middle 1970's. There is every reason to suppose that further studies on these lines will lead to the creation of new highly selective catalytic methods for the synthesis of carbonyl and other oxygen-containing compounds.

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During the preparation of the review for the press, additional data were published in the literature. In particular, the oxallyl complexes of molybdenum, tungsten, and rhenium were synthesised from α-chloroketones.[159] Titanium(IV) enolates have been obtained by treating aliphatic ketones, aldehydes, and carboxylic acid esters or amides with $Cp_2Ti{=}CH_2$.[160] The isomerisation of an acyl complex of iron in a primary aliphatic alcohol in the presence of $HOSO_2CF_3$ resulted in the synthesis of the corresponding oxallyl complex.[161] The oxallyl complexes of rhodium(III) have been

obtained by the reaction of aliphatic alkanones with octaethylporphyrin complexes of rhodium.[162,163] The oxallyl complexes of ruthenium(II) (mixture of two stereoisomers) have been synthesised by the reaction of $HRuCl(CO)(PPh_3)_3$ with dimethyl fumarate.[164]

A review has been devoted[165] to the isomerisation of 1,2-epoxides in the presence of phosphine complexes of rhodium(I) and iridium(I).

Cerium enolates, obtained from the corresponding lithium enolates derived from ketones, react with alicyclic ketones or aromatic aldehydes at −78 °C, forming a *threo*-aldol in more than 90% yield[166] (when zirconium enolates are used, mainly the *erythro*-aldol is obtained[101,102]). The aldol condensation of vinyl ketones with aldehydes at 40–110 °C in the presence of $HRh(PPh_3)_4$ affords β-hydroxy-α-methyleneketones in 30–460% yield relative to the catalyst.[167]

The interaction of lithium or rhodium enolates derived from ketones or carboxylic acids with esters of αβ-unsaturated acids or with vinylketones in the presence of iron carbonyls leads to carboxylic acid esters substituted by a functional group in the β-position.[168–170]

A convenient method of synthesis of heterocyclic compounds involves the intramolecular alkylation of unsaturated esters or amides of α-halogeno-substituted carboxylic acids, catalysed by zerovalent palladium or nickel complexes.[171–173] The palladium complexes are more effective in this reaction than the nickel complexes.

Another example of the intramolecular alkylation is provided by the synthesis of bicyclic ketones from the trimethylsilyl ethers of the enols of α-allylcyclohexanones catalysed by $Pd(OAc)_2$.[174]

The reaction of $PPh_3$ with CO and acetone, catalysed by $[RhCl(CO)_2]_2$ led to the synthesis of α-benzylacetone in a yield of 2.2–11 moles per mole of the catalyst.[175]

Depending on the conditions, the stoichiometric reaction of 1,1-dibromocyclopropanes with $Ni(CO)_4$ leads to cyclopropanecarboxylic acid esters or amides or the corresponding γδ-unsaturated derivative.[176–178]

αβ-Unsaturated bicyclic ketones have been obtained by the intramolecular cyclisation of alkeneacetylenic [vinyl ethynyl?] ethers with participation of $Co_2(CO)_8$ and CO.[179]

The reaction of vinyl triflates with acrylic monomers, which results in the formation of β-cyclohexenyl-substituted αβ-unsaturated carboxylic acid aldehydes, esters, or amides, proceeds via a stage involving the formation of intermediate oxallyl complexes.[180]

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# Intramolecular [4 + 2] Cycloaddition

M.S.Salakhov and S.A.Ismailov

The results of studies in intramolecular [4 + 2] cycloaddition carried out in recent years are surveyed. The synthetic possibilities of this reaction for the preparation of natural products and its high stereoselectivity and regioselectivity are demonstrated. The differences and similarities between intramolecular and intermolecular [4 + 2] cycloaddition reactions are elucidated.
The bibliography includes 207 references.

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## I. INTRODUCTION

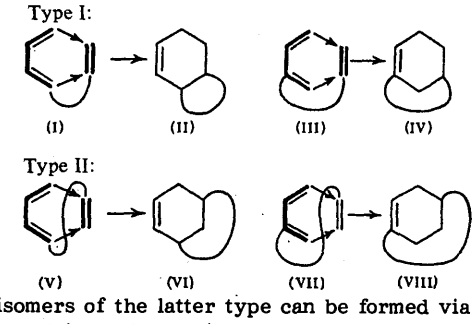
The study of the intramolecular [4 + 2] cycloaddition {IAMC[4 + 2]} reaction has attracted much attention by investigators[1-3] owing to the specific possibilities of the synthesis of polycyclic natural products, in particular sesquiterpenes, antibiotics, alkaloids, vitamins, etc., with its aid[4] and also because of its high stereoselectivity and regioselectivity which makes it possible to synthesise many skeletal structures which are difficult to obtain by other methods.[5-11] Although it is believed[1-3] that the first IAMC[4 + 2] reaction was described in 1953 by Alder,[12] who discovered the diene synthesis in 1928,[13] one should note that it was known as early as 1948 in relation to the Diels–Alder intramolecular reaction of cyclooctatetraene.[14] The existing reviews in the literature[1-3] devoted to the IAMC[4 + 2] reaction cover the period between 1953 and 1978. After the appearance of these reviews, the number of publications on this field increased greatly. In these communications attention was concentrated on the treatment of the mechanism of this type of cycloaddition characterised by the concerted but non-synchronous formation of bonds, by supra- and also antara-facial interactions of the orbitals, the reactivity and selectivity of the interacting components, the influence of the side chain linking the diene and the dienophile on the structure of the transition state (TS), the influence of catalysts on the stereoselectivity and regioselectivity of the reaction, etc.

These and other problems are important for the elucidation of the mechanism of the Diels–Alder reaction in general and the IAMC[4 + 2] reaction in particular. In the present review we attempted to examine these problems concentrating attention on the publications covering the period 1979–1983.

## II. CHARACTERISTIC FEATURES OF INTRAMOLECULAR-[4 + 2]CYCLOADDITION

### 1. Stereoselectivity and Regioselectivity

Depending on the site where the dienophile fragment is linked to the diene fragment, the IAMC[4 + 2] reaction can lead to the formation of different isomers.[15] The different orientations of the reacting fragments in the TS [(I) or (V), (III) or (VII)] create additional possibilities for the formation of different regioisomers [(II) and (VI), (IV) and (VIII)]:




Regioisomers of the latter type can be formed via four pathways: (a) by the *s*,*s*-interaction of the HOMO of the diene and the LUMO of the dienophile; (b) by the *a*,*a*-interaction of the LUMO of the diene and the HOMO of the dienophile; (c) by the *a*,*a*-interaction of the HOMO of the diene and the LUMO of the dienophile; (d) by the *s*,*s*-interaction of the LUMO of the diene and the HOMO of the dienophile (Fig.1). However, the *s*,*s*-interactions (a) and (d) are geometrically unfavourable compared with the *s*,*s*-interactions for the TS (I) and (III).

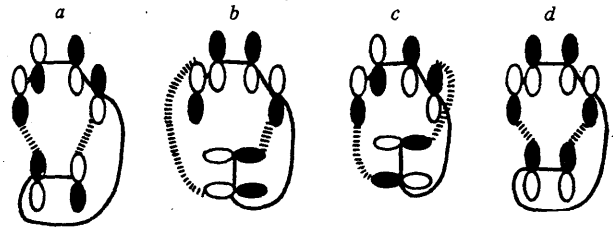
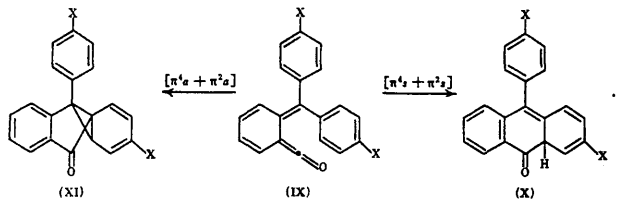



Figure 1. The possible pathways in the interaction of the diene and dienophile orbitals on formation of the regioisomers (VI) and (VIII).

It is noteworthy that, by virtue of the presence of bridging chains of atoms between the diene and dienophile fragments, the TS for the IAMC[4 + 2] is electronically asymmetric and

the coefficients of the atomic orbitals of the diene and dienophile fragments should be different. This determines the *s,s*- or *a,a*-interaction between the diene and dienophile orbitals[16] and also the regioselectivity of the cycloaddition. The higher coefficients for C(4) and C(2′) and also for C(1) and C(1′) favour the *a,a*-interaction of the orbitals, while the higher coefficients for C(1) and C(2′) or C(1′) and C(4) favour the *s,s*-interaction, which is a feature distinguishing the regioselectivity of the IAMC[4 + 2] from the intermolecular [4 + 2]cycloaddition {IRMC[4 + 2]} (Fig. 2).

Thus knowing the structure of the final adduct, the HOMO and LUMO energies of the diene and the dienophile, and the coefficients of the atomic orbitals, it is possible to infer readily the pathway followed in the interaction of the orbitals. As an example, one may quote the IAMC[4 + 2] of the triene (IX), where norcaradiene (XI) was discovered instead of the expected product (X):[17,18]

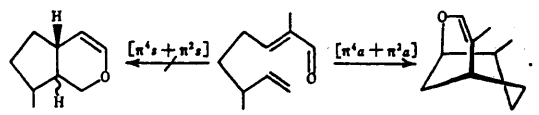



(XI) (IX) (X)

The introduction of the electron-donating dimethylamino-substituent X increases the coefficient of the HOMO in the *p*-position in the benzene ring. On the other hand, the central carbon atom of the keten group, located in the plane of the π* orbitals, is electrophilic, so that the cycloaddition entails the formation of a bond between this atom and the *p*-carbon atom of the *NN*-dimethylaminophenyl group (Fig. 3).

Calculation of the total energy and of the coefficients of the frontier orbitals of the atoms in terms of the CNDO/2 approximation demonstrated that the HOMO of *NN*-dimethylaniline and the LUMO of the unsaturated keten differ little as regards energy and that the interaction between the corresponding fragments therefore gives rise to additional stabilisation in the TS in the cyclisation of the triene (IX).

The IAMC[4 + 2] of 2,6-dimethylocta-2,7-dienal (XII) using $BF_3$ as the catalyst affords a 47% yield of *exo*-4,8-dimethyl-2-oxabicyclo[3.3.1]non-3-ene (XIII), which is an intermediate in the synthesis of iridiomyrmycene—the insecticidal iridoid isolated from *Iridomyrmex himilus*:[19]




(XIV) (XII) (XIII)

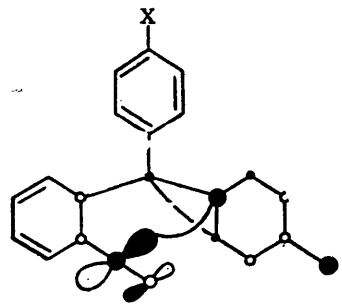



**Figure 3.** The antarafacial interaction of the orbitals in compound (IX).

The catalyst apparently reduces the LUMO of the dienal in this reaction as a consequence of the formation of the complex[20] and thus favours the *a,a*-interaction of diene and dienophenyl orbitals, which results in the formation of the product (XIII) and not (XIV).

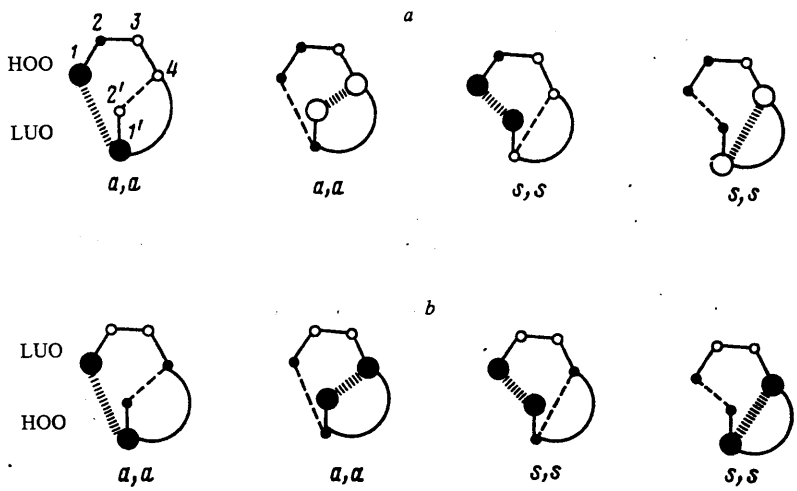
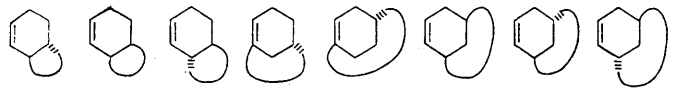
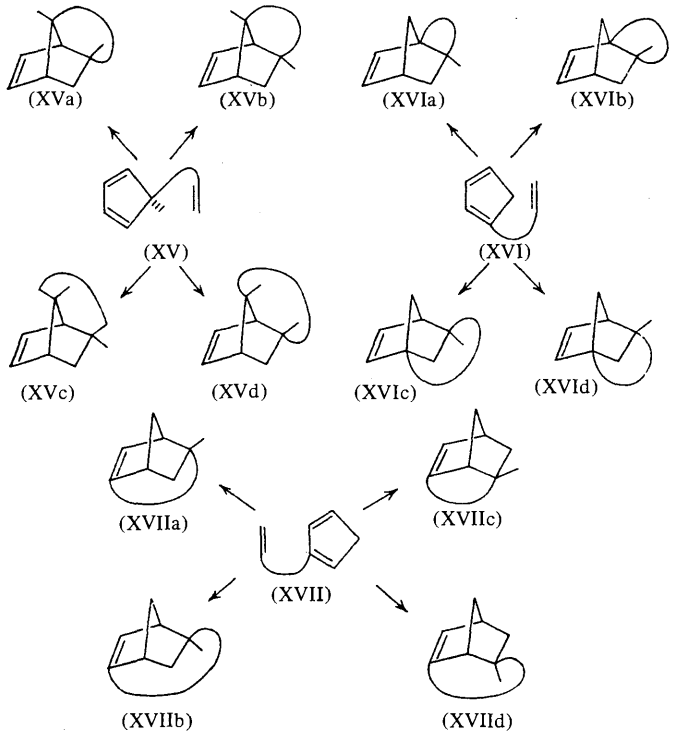



**Figure 2.** The regiospecificity in IAMC[4 + 2]; schematic representation of the atomic coefficients of the diene (*a*) and dienophile (*b*) orbitals.

The structure of the TS in the cycloaddition reaction and the establishment of a particular configuration in the junction of the rings (*cis*- or *trans*-, *endo*- or *exo*-) undoubtedly depend on the *E*- or *Z*-configuration of the initial trienes. The trienes containing the buta-1,3-diene fragments can give rise to eight stereoisomers when account is taken of the *trans*- and *cis*-junctions in the adducts:



For the triene consisting of cyclopentadiene and ethylene fragments, one may expect formally the formation of twelve structures:

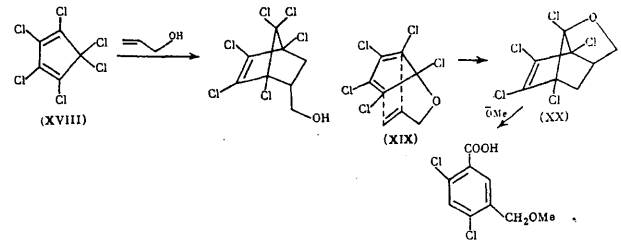



In contrast to the other structures, the formation of the isomers (XVa), (XVd), (XVIc), (XVIIb), and (XVIId) requires the twisting of the linking bridge chain.

## 2. Structure and Reactivity

It is self-evident that the structure of the substrate not only influences the stereochemistry of the reaction but also determines the substrate reactivity in the reactions investigated and the reactivities of the given reactant in different reaction series are therefore different. This leads to the question of the difference between the reactivities of the same diene in the IAMC[4 + 2] and IRMC[4 + 2] processes.

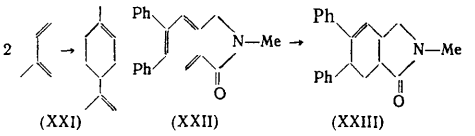
It is known[21] that the IRMC[4 + 2] of hexachlorocyclopentadiene (XVIII) to allyl alcohol proceeds under fairly severe conditions (125 °C, two days, sealed tube), while 5-allyloxy-1,2,3,4,5-pentachlorocyclopentadiene (XIX), obtained by nucleophilic substitution in the diene (XVIII) on treatment with allyl alcohol, is converted spontaneously into the final product (XX) at room temperature:[22]



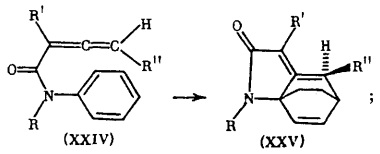

A new rearrangement was observed on treatment of compound (XX) with sodium methoxide.[23]

The presence of substituents in the dienophile component of the triene does not prevent the occurrence of the IAMC[4 + 2] reaction. In this case steric factors probably predominate.

It is known[25] that the entropies of activation for pericyclic reactions, including IRMC[4 + 2], play a major role and that an increase of their negative values indicates a greater order in the system. It was expected that the TS in the IAMC[4 + 2] reaction would be more ordered than for the IRMC[4 + 2] reaction. However, there are virtually no suitable examples of such a comparison in the literature. Comparison of the $\Delta S^{\neq}$ for the dimerisation of isoprene and the IAMC[4 + 2] reaction of compound (XXII) to give the product (XXIII) showed that the value of $\Delta S^{\neq}$ obtained for the dimerisation of isoprene is more negative than for the reaction (XXII) → (XXIII) (−41 and −14.4 e.u. respectively), which is unexpected[2] and is apparently due to the non-synchronous formation of bonds in the IAMC[4 + 2].[26–29]

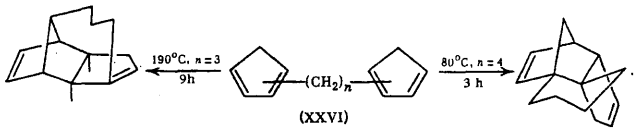



The IAMC[4 + 2] of the allene fragment to the benzene ring in compound (XXIV) proceeds readily with formation of the product (XXV), although such a thermal reaction is forbidden for IRMC[4 + 2]:[30]




R = Me, H, Ph;
R' = Me, H, $SiMe_3$;
R'' = H, $SiMe_2Ph$.

It is essential to take into account the fact that IAMC[4 + 2] does not always proceed at a higher rate than IRMC[4 + 2]. For example, the dimerisation of cyclopentadiene takes place readily at room temperature,[31] but the IAMC [4 + 2] of the polymethylenecyclopentadienes (XXVI, $n = 0 - 12$),[32] requires more severe conditions:




It follows from the data in Table 1 and the information contained in the earlier reviews[1–3] that the reactivity of the trienes is significantly determined by the length and conformational characteristics of the bridge chain linking the diene and dienophile fragments in the triene.

## III. THE FORMATION OF ANNELATED SYSTEMS

### 1. The 6/5-Annelated System

Vigorous study of the formation of the 6/5-annelated cyclic system (condensed rings consisting of six- and five-membered fragments) is being prosecuted mainly by three groups of investigators.[39–44,49–53]

In order to study the possibility of the total synthesis of (±)-dendrobine, the stereochemistry of the IAMC[4 + 2] of methyl (*E*,*E*,*E*)- and (*Z*,*E*,*E*)-6-alkoxy-11-methyldodeca-2,7,9-trienoates (XXVII) and (XXVIII) was examined:[39]

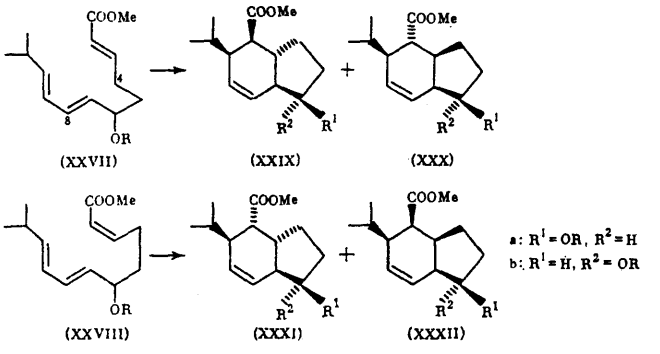
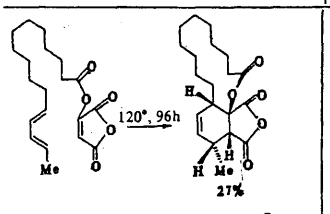
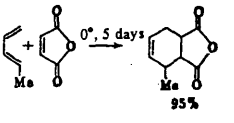
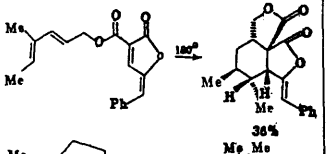
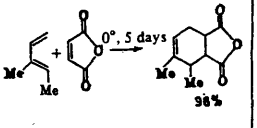
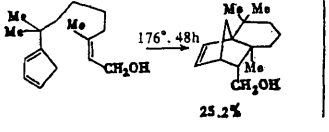
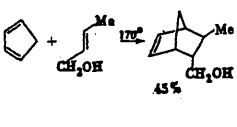
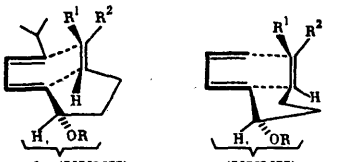



Table 1. The influence of the side chain connecting the diene and the dienophile on the parameters of IAMC[4 + 2] compared with IRMC[4 + 2].

| IAMC[4 + 2] | Refs. | IRMC[4 + 2] | Refs. |
|---|---|---|---|
|  | [33] |  | [36] |
|  | [34] |  | [37] |
|  | [35] |  | [38] |

It was established that in all cases *trans*-hexahydroindene rings [compounds (XXIX) and (XXXI)] are formed to a greater extent than the *cis*-isomers (XXX) and (XXXII). A decrease of the reaction temperature favours the formation of the *trans*-isomers (XXIX) and (XXXI). The TS in the boat form, which leads to the formation of the isomers (XXXIIa, b) is unfavourable owing to the steric interaction between the H atoms of the C(8) atom and the OR group, which accounts for the ratio (XXX)/(XXXII) found in the reaction products. Analysis of the molecular model showed that such geometry is more readily achieved in the TS leading to the *trans*-joined products [*endo*-(XXVII) and *exo*-(XXVIIIa)] than in the TS leading to the *cis*-joined products [*exo*-(XXVII) and *endo*-(XXVIIIa)].




*endo*-(XXVII) *exo*-(XXVII)
*exo*-(XXVIIIa) *endo*-(XXVIIIa)

This effect is believed to be sufficiently large to compete with Alder's *endo*-rule in determining the stereochemical consequences of the cyclisation of the triene (XXVIIIa).

The predominance of the *trans*-isomers (XXXVII), (XXXVIII), (XXXIX), and (XL) is also observed in the IAMC[4 + 2] of methyl deca-2,7,9-trienoates (XXXIII), (XXXIV), (XXXV), and (XXXVI) (Table 2).[40,41]

Table 2. IAMC[4 + 2] of methyl deca-2,7,9-trienoates.[40,41]

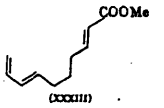
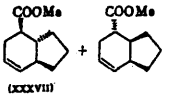
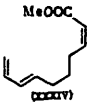
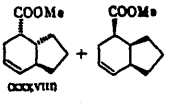
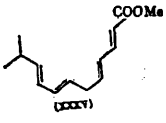
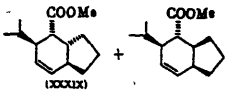
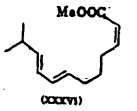
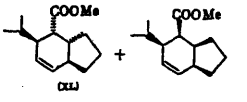
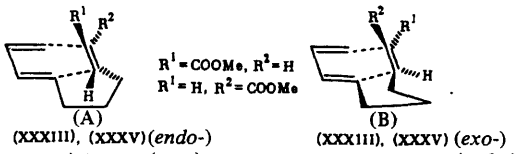
| Trienes | Conditions | Products | Yield, % | *trans*/*cis* |
|---|---|---|---|---|
|  (XXXIII) | 150°, 24h |  (XXXVII) | 65 | 60:40 |
|  (XXXIV) | 180°, 5h |  (XXXVIII) | 75 | 65:35 |
|  (XXXV) | 150°, 40h |  (XXXIX) | 72 | 72:28 |
|  (XXXVI) | 180°, 5h |  (XL) | 75 | 67:33 |

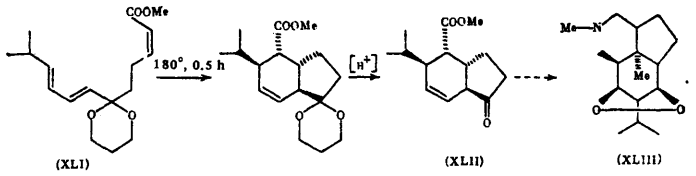
Table 2 shows that the selectivity for the *trans*-joined adducts does not in essence depend on the stereochemistry of the dienophile and the *endo*-rule is undoubtedly a consequence of the cyclisation of the trienes (XXXIV) and (XXXVI). The secondary orbital interaction does not influence the consequences of the cyclisation of the *trans*-trienes (XXXIII) and (XXXV), since it stabilises the *endo*-TS. The breakdown of the *endo*-rule may be a consequence of the strain in the TS (B) compared with (A), which hinders the formation of the boat conformation of the cyclohexene ring in the TS (B).

Furthermore, steric interactions between the hydrogen atoms of the methylene group in the 4-position and of the methylidyne group in the 8-position are observed only for

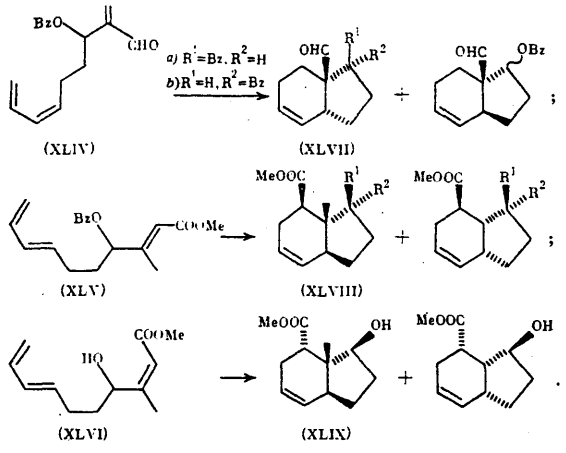
the TS (B), where these atoms are in the eclipsed positions.



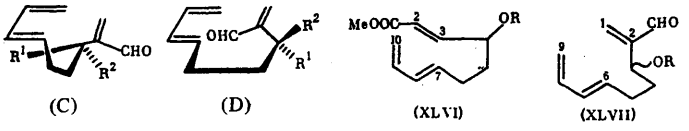

The unusual *trans*-stereoselectivity of the IAMC[4 + 2] for the triene (XLI) ensured the success of the key stage in the improved synthesis of hexahydroindenone (XLII), which is a precursor of dendrobine (XLIII): [42,43]



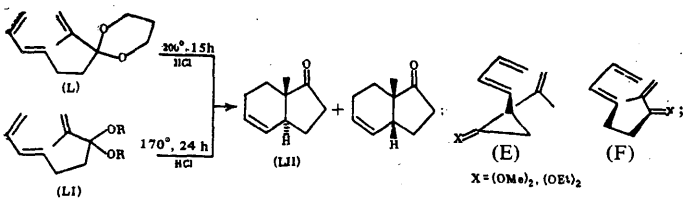

The IAMC[4 + 2] of the angularly methyl-substituted trienes (XLV) and (XLVI) also gives rise predominantly to the *trans*-isomers (XLVIII) and (XLIX); [44] the adducts obtained are important structural elements in the synthesis of derivatives of vitamin D:




It is of interest that the cyclisation of compound (XLIV) exhibits the opposite behaviour—preferential *cis*-selectivity. The main product derived from the triene (XLIV) is obtained from the TS (C) in which the aldehyde group occupies an *exo*-position relative to the diene. However, the *cis*-joined TS (C) is energetically less favourable than the *trans*-(D). It has been established that the LUMO coefficients for C(1) and C(9) are higher than for C(2) and C(6). This fact is crucial in the formation of the *cis*-isomer (XLVII) and the concerted rather than the synchronous interaction of the orbitals of the diene in the dienophile is therefore preferable.

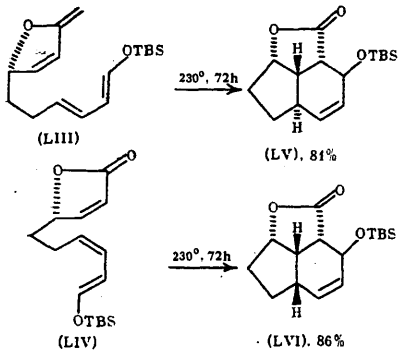



The preferable formation of the angularly substituted *trans*-hydroindenone (LII), containing an oestrogen fragment, is observed in the thermolysis of the trienes (L) and (LI): [45,46]

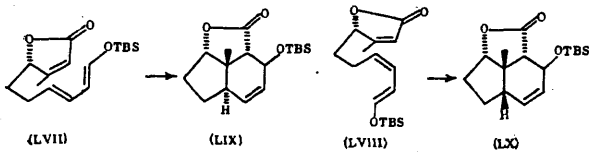



The *endo*-TS (E) is characterised by an appreciable steric hindrance owing to the interaction between one of the alkoxy-groups and the butadiene system, where the corresponding *exo*-TS (F) is more stable.

The *trans*-hydroindene system, which is a synthon for 11-deoxyprostaglandin and 11-ketosteroid, has been synthesised from the triene (LIII) and (LIV): [47]

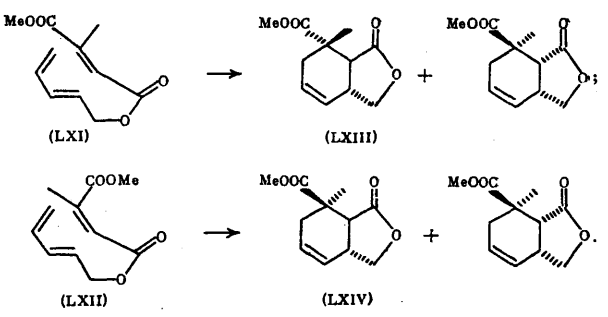



It is of interest that the *E*,*E*-triene (LIII) affords only the *trans*-product (LV), while the cyclisation of the *E*,*Z*-triene (LIV) leads exclusively to the *cis*-isomer (LVI). The results of investigations have demonstrated the preferential *exo*-orientation of the butenolide fragment in the TS for the cyclisation reaction. The angularly methyl-substituted analogues of these trienes also react entirely stereoselectively, i.e. *E*,*E*-(LVII) → (LIX) and *E*,*Z*-(LVIII) → (LX):



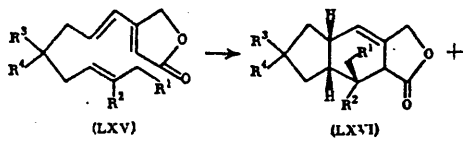

It has been suggested that the rigid structure of the butenolide promotes the necessary orientation of the dienophile in the TS in view of the stereoselectivity of the IAMC[4 + 2] reaction.

The IAMC[4 + 2] of the esters of mesoconic acid (LXI) and sorbyl citraconate (LXII) gives rise preferentially to the *trans*-isomers (LXIII) and (LXIV): [48]



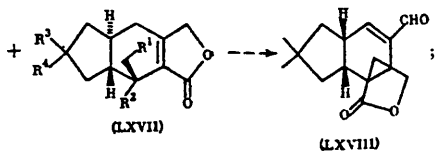

The *trans*:*cis*-ratio is 4.3:1.

The *trans*-stereoselectivity of the cyclisation is also observed in the IAMC[4 + 2] of the triene (LXV), which leads to the synthesis of marasmic acid (LXVIII)—a sesquiterpene antibiotic: [49–51]



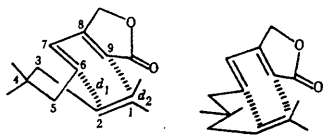
(LXV) (LXVI)

$R^3 = R^4 = Me$
$R^1 = COOMe, CN, COOBu$
$R^2 = H, COOMe, CN$



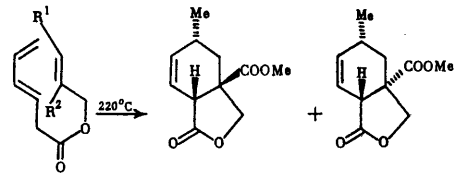
(LXVII) (LXVIII)

The main requirement for the formation of *trans*-hydroindenes is the non-bonding interaction of the diene and dienophile fragments, which leads to an asymmetric TS. The secondary orbital interaction is energetically incapable of overcoming the unfavourable non-bonding interactions in the TS, which leads to the *cis*-isomer:



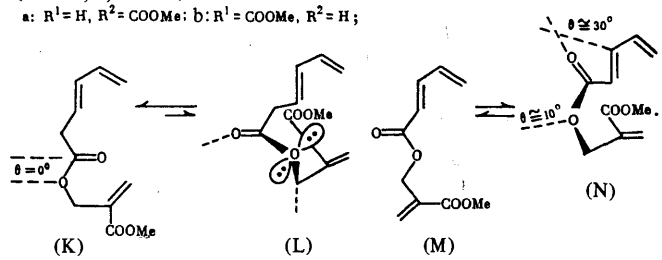
The absence of a steric effect of the substituents on the stereochemistry of the cyclisation can be accounted for by the asymmetric TS in which the distance $d_1$ between the C(6) and C(2) atoms is smaller than the distance $d_2$ between the C(9) and C(1) atoms. This is due to the greater coefficients of the MO at C(2) than at C(1) as a consequence of the strong polarisation of the dienophile fragment of the molecule by the substituents at C(1). Kinetic data have shown that the rate of cyclisation is strongly influenced by the nature of the substituents in the triene. The higher rate of cyclisation when the substituent COOR is used at C(1) compared with CN is consistent with literature data[52] concerning the influence of the substituents (COOR > CN) on the rate of IRMC[4 + 2]. The relatively smaller increase of the rate of reaction by the second substituent COOR at C(1) compared with CN can be explained by the steric inhibition of the resonance as a consequence of the impossibility of a coplanar disposition of the two COOR groups and the C=C bond. It is assumed that the lower rate of cyclisation of the triene (LXV, $R^3 = R^4 = Me$) to the *trans*-hydroindene (LVII) compared with the corresponding *cis*-isomer is due to the fact that the introduction of the methyl groups into the connecting chain increases the fraction of the cisoid conformers with a disposition of the diene and dienophile favourable for cyclisation, which decreases $\Delta S^{\neq}$ by approximately 3 e.u.

The influence of the structure of the connecting chain on the formation of products has also been demonstrated in relation to the reactions of the trienes (LXIXa, b).[53] In both cases the IAMC[4 + 2] led to γ-lactones instead of the expected δ-lactones and the nature of the rearrangement is obscure:



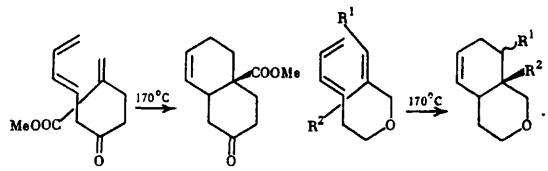
(LXIXa, b) (LXXa)

a: $R^1 = H$, $R^2 = COOMe$; b: $R^1 = COOMe$, $R^2 = H$;



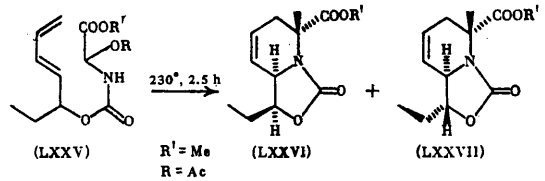
(K) (L) (M) (N)

It is believed that the rearrangement of the double bonds in the trienes (LXIXa, b) is the rate-limiting stage of the reaction. In the case of the TS (L) the dihedral angle between the π-system of the CO group and the unshared electron pair of oxygen should be 90°, which prevents the overlap of diene and dienophile orbitals. On the other hand, in the case of the TS (N) there are no such limitations and the IAMC[4 + 2] takes place readily. In order to confirm this, the IAMC[4 + 2] of the model compounds (LXXI) and (LXXIII), in which there is no ester group and hence there is no orbital interaction between the π-system of CO and the unshared electron pair at the oxygen atom, has been carried out. As was to be expected, this results in the formation of the cyclisation products (LXXII) and (LXXIV), which indicates the decisive role of the above interactions in the stereocontrol of the IAMC[4 + 2]:



(LXXI) (LXXII) (LXXIII) (LXXIV)

In order to synthesise the spermidine alkaloids such as palustrine and anhydrocannabisativine, the IAMC[4 + 2] reactions of the triene (LXXV) have been investigated and it has been shown that its thermolysis proceeds entirely stereoselectively with formation of a mixture of the *trans*-products (LXXVI) and (LXXVII): [54–56]

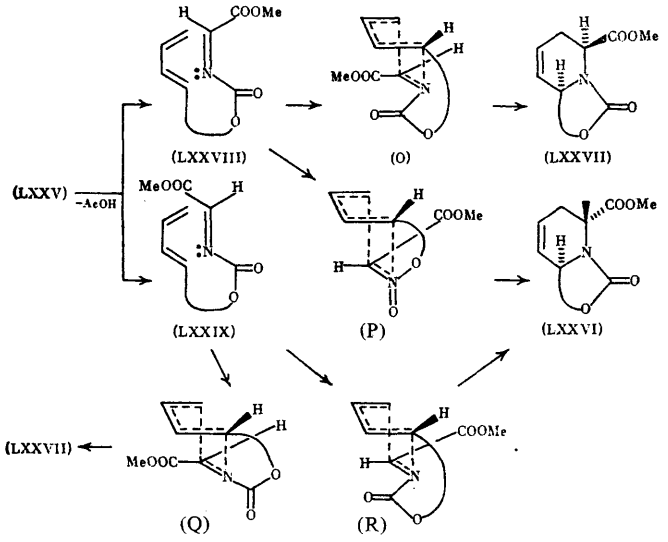


(LXXV) (LXXVI) (LXXVII)

$R' = Me$, $R = Ac$

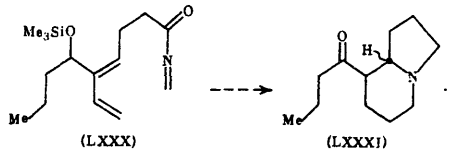
The yield is 59% and the isomer ratio is 55–45. It is assumed that the precursors of the products (LXXVI) and (LXXVII) may be the Z-imine (azamaleate) (LXXVIII) or the E-imine (azafurmarate) (LXXIX) obtained by the elimination of AcOH in the thermolysis of the diene (LXXV); the imines

give rise to the corresponding cycloaddition products:

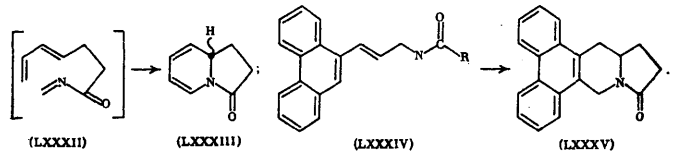



In contrast to Roush's hypotheses, the authors of the above studies[54–56] assume that the length of the bridging chain does not influence the stereochemistry of the final products and the *exo*-azamaleate TS (P) is energetically preferable to the TS (O). The TS (O) does not lead to the expected product; for this reason, the formation of the azamaleate in this process is rejected; the authors[54–56] suggest that the secondary orbital interaction between the CO group at the nitrogen atom and the diene component of the molecule is responsible for the stereocontrol of the cyclisation and that the latter proceeds via the azafumarate (LXXIX), which leads to the TS (I).

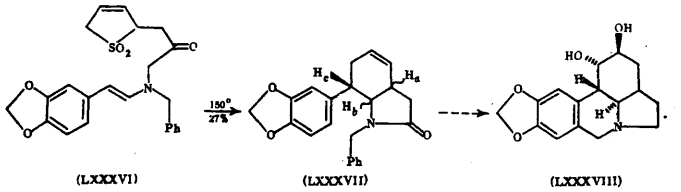
The IAMC[4 + 2] of the suggested intermediate dieneacylimine (LXXX) is the key stage in the synthesis of the alkaloid eleokanine A (LXXXI):[57]



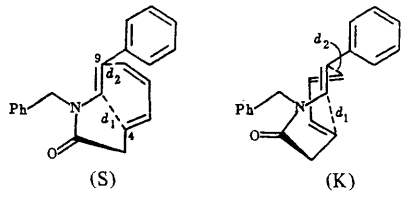

Two indolizidine alkaloids—α-coniceine (LXXXIII) and tylophorine (LXXXV)—have also been synthesised by the IAMC[4 + 2] of the trienes (LXXXII) and (LXXXIV):[58]




The *trans*-stereoselectivity of the cyclisation has been also observed in the synthesis of the antibiotic lycorine (LXXXVIII) from the triene (LXXXVI), as described by Martin et al:[59]

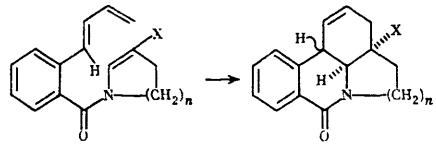



In order to interpret the stereochemical consequences, models of the concerted cycloaddition with an asymmetric biradical or zwitter-ionic TS have been considered.



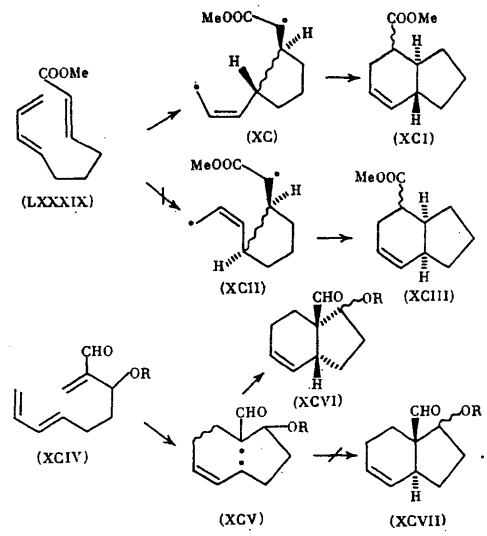

The relative rate of cycloaddition depends on the stabilisation of the radical centre by neighbouring groups. If the aryl substituent at C(9) stabilises the free radical to a greater extent than the nitrogen atom at C(8), the formation of the C(4)–C(8) bond will be preceded by the formation of the C(1)–C(9) bond, i.e. $d_2 < d_1$ for the TS (K). Thus one can predict the stereochemistry of the cyclisation; in the case considered the *trans*-stereoselectivity of the reaction is observed and the TS (S) should lead to a *cis*-joined product.

The galanthan system, which constitutes the nucleus in many *Amaryllidacaea* alkaloids, has been synthesised with the aid of IAMC[4 + 2] in accordance with the scheme[60]



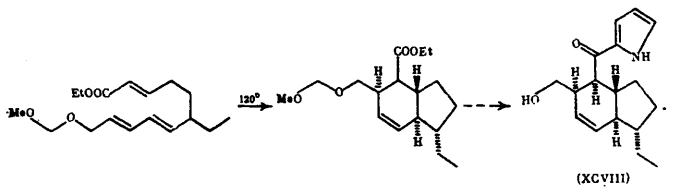
$n = 1, 2$; X = COOMe.

The biradical character of the TS in the IAMC[4 + 2] reaction has also been investigated in relation to the trienes (LXXXIX) and (XCIV):[61]



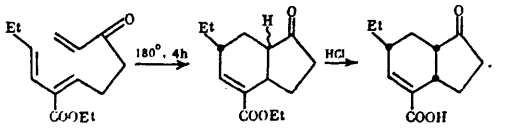

The preferential formation of the *trans*-isomer (XCI) from the triene (LXXXIX) and the *cis*-isomer (XCVI) from the triene (XCIV) can be accounted for by a concerted rather than synchronous TS in the cyclisation reaction; in particular, the "zigzag" TS (XCII) is energetically more favourable than the TS (XC). If the bonds are formed non-synchronously in the cyclisation of the triene (XCIV), then the TS should assume the configuration of a nine-membered ring. This is a state in which the steric strain in the formation of *cis*-hydroindene is reduced to a minimum.

The "right-hand" half of the new ionophore antibiotic X-14547A (XCVIII) is obtained in a high yield [62] from the *trans*-hydroindene:



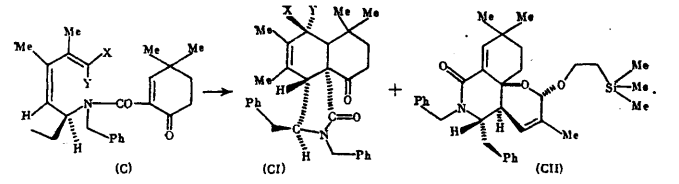
(XCVIII)

(±)-Coronafacic acid (XCIX), isolated from the culture medium of *Pseudomonas coronafacience*, is a structural fragment of the phytotoxin coronatine and is obtained from the hydroindene system in an overall yield of 7%: [63,64]



(XCIX)

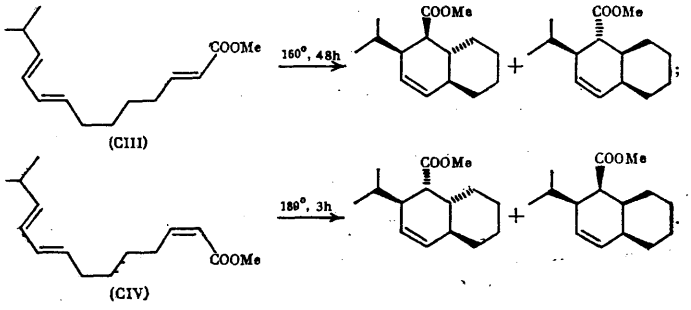
IAMC[4 + 2] constitutes a novel method of synthesis of chiral compounds; in particular the cyclisation of the chiral trienes (C a, b) (a: X = Y = H; b: X = $OCH_2CH_2SiMe_3$; Y = H or $OCH_2CH_2SiMe_3$) proceeds stereo- and enantioselectively,[65-67] as a result of which the product (CIa, X = Y = H) is obtained from the triene (Ca), while the triene (Cb) gives rise to a mixture of the products (CIa, X = $CH_2$ – $CH_2SiMe_3$, Y = H) and (CII), which are precursors of cytochalasin *C*:



(C) (CI) (CII)

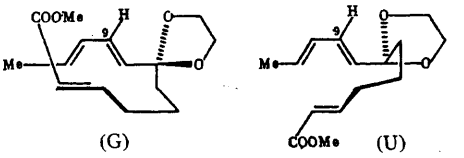
## 2. The 6/6-Annelated System

The formation of the 6/6-annelated system is to some extent stereochemically different from the formation of the 6/5-system. In the total synthesis of chlorothricin, it was observed that the IAMC[4 + 2] of the 2,8,10-trienoates (CIII) and (CIV) leads preferentially to *cis*-joined products: [68]



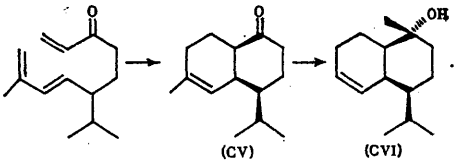
(CIII) (CIV)

Examination of Dreiding molecular models of the *cis*- and *trans*-TS (G) and (U) showed that the eclipsed 1,3-interaction between the H atom at C(9) and the OR group at C(7) develops in the *trans*-TS (G), while it is absent in the *cis*-TS (U). This interaction explains fairly satisfactorily the increasing selectivity also for other undecatrienes having substituents at C(7).



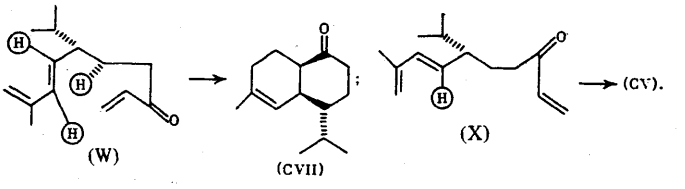
(G) (U)

The synthesis of a crystalline sesquiterpene alcohol (±)-torreyol (CVI) also proceeds via the formation of the *cis*-joined product (CV): [69]



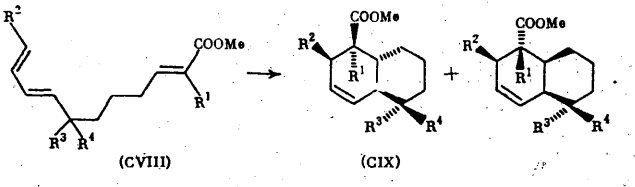
(CV) (CVI)

The formation of the *cis*-isomer (CV) and not the *trans*-isomer (CVII) can be accounted for by the steric hindrance in the TS (W) ("chair"), because the isopropyl group is in the *syn*-position relative to the angular H atom; on the other hand, in the TS (X) ("boat") such hindrance is absent:



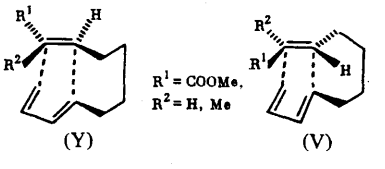
(W) (CVII) (X) (CV).

The characteristics of the stereochemistry of the IAMC[4 + 2] of various trienes (CVIII, $R^1$ = Me, $R^2$ = H, Me, $R^3$ = $R^4$ = OAlk, $R^3$ + $R^4$ = $OCH_2CH_2O$) make it possible to synthesise the chlorothricolide (CIX)—a fragment of the molecule of chlorothricin produced by a culture of *Streptomyces antibioticus*: [70]



(CVIII) (CIX)

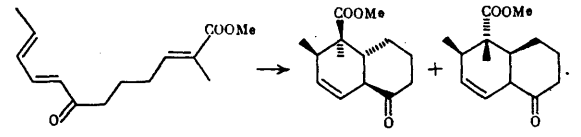
The following features were demonstrated: (a) the somewhat unexpected preferential formation of *cis*-joined products; (b) the absence of a dependence of the reaction selectivity on the stereochemistry of the dienophiles; (c) the independence of the stereochemical reaction pathway of the secondary orbital interaction. In most cases the main products are formed via a TS of type (Y). Consequently the *endo*-group breaks down in the reactions of *E,E,E*-trienes:



(Y) (V)

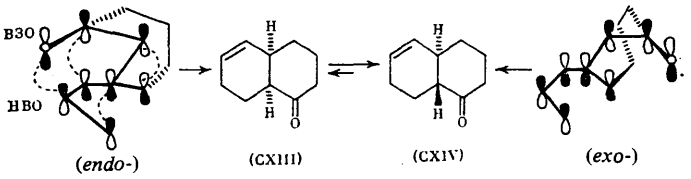
It has been established that the cyclisation is kinetically controlled. One should therefore assume that the *cis*-joined TS (Y) has a somewhat lower energy than the *trans*-joined TS (V) (by 1.0–1.2 kcal $mol^{-1}$). In all cases the selectivity depends strongly on fine steric conformational effects. Another well known factor influencing the stereochemical

consequences of the IAMC[4 + 2] is the nature of the hybridisation of the atoms or atomic groups in the chain connecting the diene and the dienophile.[71] The $sp^2$-hybridised atoms in the allyl position in the diene increase the coplanarity of the latter in the reaction TS; thus the orbitals overlap along the reaction coordinate. The $sp^2$-hybridisation in the allyl position in the diene leads to a result opposite to that of the $sp^3$-hybridisation, which has been confirmed[71] in relation to the cyclisation of the diene (CX):



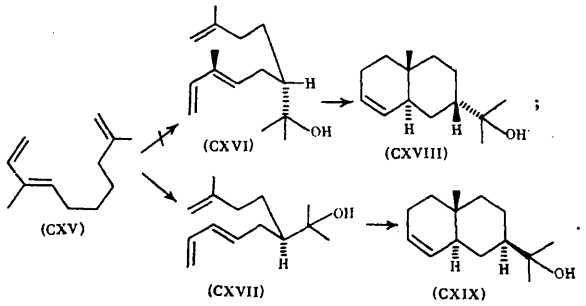

(CX) (CXI) (CXII)

The (CXI):(CXII) ratio is 65:35. Inspection of Dreiding models suggested that the C=O group becomes coplanar with the butadiene fragment; thus the above configuration can be readily obtained only for the transoid disposition, which leads to the preferential formation of the *trans*-joined product (CXI). In order to explain this, the secondary orbital interaction favouring the *endo*-TS has been invoked to account for this phenomenon in a number of other similar examples.[72] The transition from compound (CXIII) to the product (CXIV), which constitutes a kinetically controlled reaction, ensures the preferential *endo*-stereoselectivity of the cyclisation with respect to the C=O group:



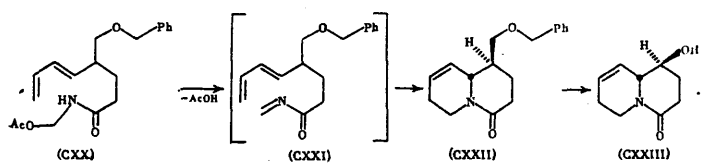

(*endo*-) (CXIII) (CXIV) (*exo*-)

The preferential formation of *trans*-joined rings has been observed in the synthesis of the crystalline sesquiterpene alcohol α-eudesmol (CXIX) from the triene (CXV) with the aid of IAMC[4 + 2].[73] By virtue of the axial position of the hydroxyisopropyl fragment in the TS (CXVI), a steric interaction of this fragment with the remainder of the molecule is observed, which does not occur at all in the case of (CXVII):



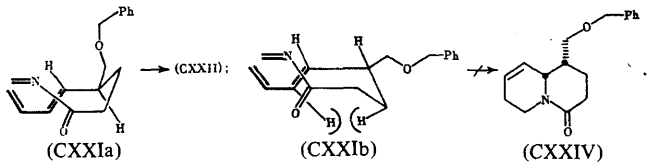
(CXV) (CXVI) (CXVIII) (CXVII) (CXIX)

In the effective synthesis of epilupinine (CXXIII), which belongs to the class of quinolizidine alkaloids, it was discovered[74] that the IAMC[4 + 2] of the triene (CXX) proceeds strictly stereoselectively via the imino-reaction pathway proposed previously:[54-56]



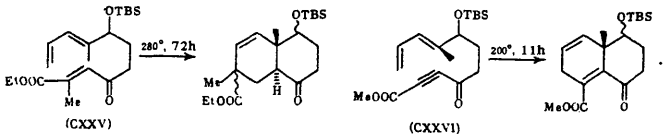

(CXX) (CXXI) (CXXII) (CXXIII)

It has been suggested that the imine (CXXI) cyclises via the TS (CXXIa). Both in the TS (CXXIa) and the TS (CXXIb), the *endo*-disposition of the C=O group is observed, so that the bulky $OCH_2Ph$ group occupies a quasi-equatorial position in the lactone ring. In the TS (CXXIa) the connecting chain assumes a quasi-boat form and such TS leads precisely to the product (CXXII). On the other hand, the lactam ring in the TS (CXXIb) assumes a quasi-chair conformation and the corresponding product (CXXIV) is not detected. Examination of the model shows that in the quasi-chair TS (CXXIb) an unfavourable non-bonding interaction takes place between the hydrogen atom in the vinyl component of the diene and the quasi-axial hydrogen atom in the connecting chain:



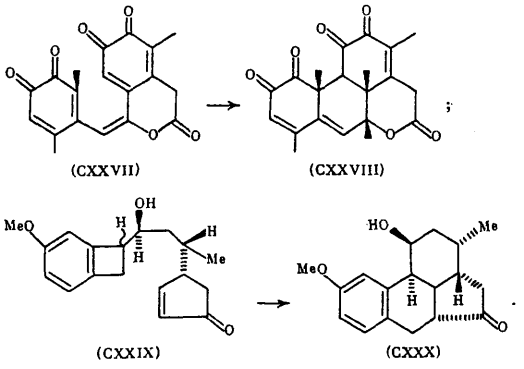

(CXXIa) (CXXIb) (CXXIV)

The *trans*-joined decalin system containing an angular methyl group, which is a structural component of terpenoids and steroid natural products, can be readily obtained[75] from the triene (CXXV) and the tetraene (CXXVI):



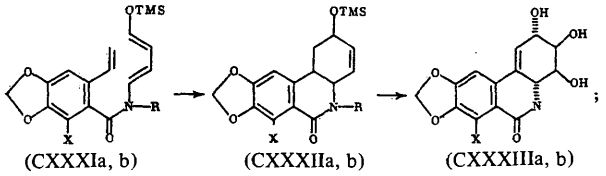

(CXXV) (CXXVI)

The diterpenoid compound quassin (CXXVIII), which contains seven asymmetric centres, can be synthesised stereoselectively from the *o*-quinone (CXXVII) by means of IAMC[4 + 2].[76] Compounds of this type are dehydrated terpenes with a high oxygen content and are present in the plants *Simaroubaceae*. Another possible pathway leading to the synthesis of compound (CXXVIII) involves[77] IAMC[4 + 2] of the benzocyclobutene derivative (CXXIX), whose product (CXXX) is converted into quassin via several stages: (CXXVII)



(CXXVII) (CXXVIII) (CXXIX) (CXXX)

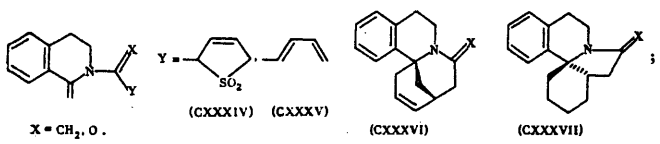
Licoricidin (CXXIIIa) and narciclasine (CXXIIIb) are of considerable interest because of their biological activity; in particular, they inhibit protein synthesis and exhibit a powerful antitumour activity. They can be readily synthesised[78] from the trienes (CXXXIa, b) by IAMC[4 + 2]:



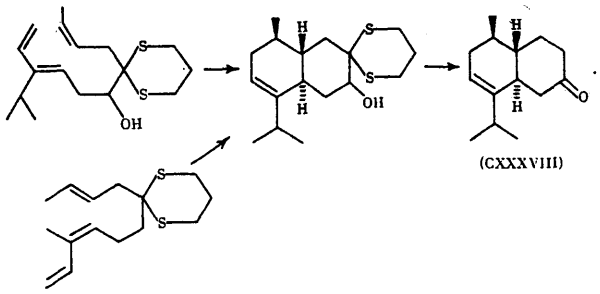

(CXXXIa, b) (CXXXIIa, b) (CXXXIIIa, b)

a: X = H; b: X = OH.

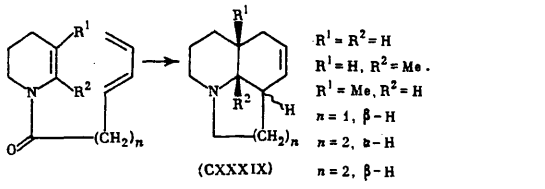
The IAMC[4 + 2] reactions of the enamines and enamides (CXXXIV) and (CXXXV) have been investigated[79,80] in order to develop a new method of synthesis of alkaloids with a tetracyclic spiran skeleton, which is characteristic of erythrin alkaloids; however, instead of the expected compound (CXXXVII), the reaction resulted in the formation of the bridged adducts (CXXXVI):



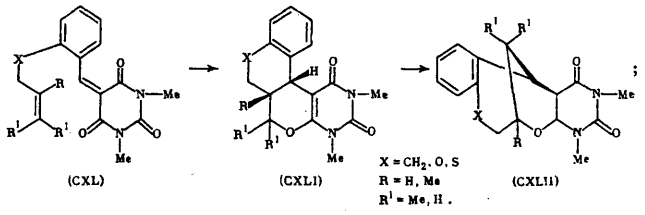

*trans*-Stereoselectivity of cyclisation has been observed in the synthesis of the cadalane sesquiterpene epizonarene (CXXXVIII) with the aid of IAMC[4 + 2]:[81]



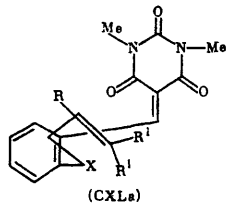

However, the *cis*-joined products (CXXXIX) are formed in the synthesis of *Aspidosperma* alkaloids:[82]



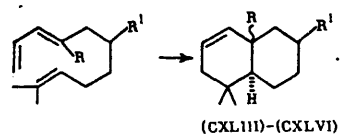

The thermolysis of the trienes (CXL) yields 20 : 1 mixtures of the products (CXLI) and (CXLII):[83]




The formation of the bridged product (CXLII) shows that the TS (CXL) has the conformation (CXLa):




A short synthesis of (±)-ambrinol (one of the components of ambergris) with the aid of IAMC[4 + 2] leads to four possible stereoisomers, namely (CXLIII, R = α-H, $R^1$ = H), (CXLIV, R = β-H, $R^1$ = Me), (CXLV, R = α-Me, $R^1$ = H), and (CXLVI, R = α-Me, $R^1$ = Me), among which compounds (CXLIII) and (CXLIV) possess the strong scent of ambergris:[84]




The IAMC[4 + 2] of the triene (CXLVII) proceeds stereoselectively with the preferential formation of compound (CXLVIII), which is converted into the angularly substituted *trans*,*anti*,*trans*-perhydrophenanthrene—(±)-fichtelite (CXLIX):[85]

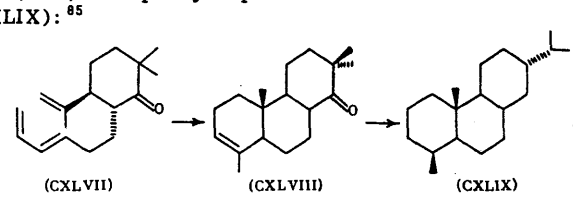
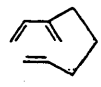
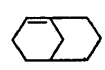
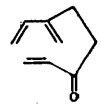
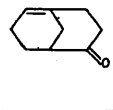
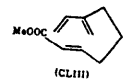
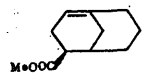
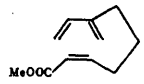
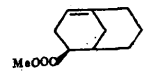
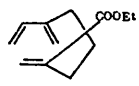
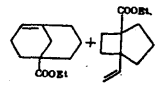



Table 3. Data for the IAMC[4 + 2] of certain trienes leading to the formation of strained bicyclo[*n*.3.1]alkenes.[15]

| Initial triene | Conditions | Products | Yield, % |
|---|---|---|---|
|  | 420°, 23 s |  | 32 |
|  | 395°, 18 s |  | 72 |
|  (CLIII) | 318°, 18 s |  | 76 |
|  (CLIV) | 365°, 12 s |  | — |
|  | 390°, 12 s |  | 50 |

The formation of bridged bicyclo[*n*.3.1]alkenes with the double bond at the bridgehead conflicts with the Bredt prohibition,[86] but, when IAMC[4 + 2] is used, this prohibition sometimes loses its force.[15] However, it has been shown that the reactivity of the triene (CL) in cyclisation is greater than that of the triene (CLI), which has been attributed to the excess strain in compound (CLII). Cycloaddition takes place with formation of the *trans*-cyclooctene ring:

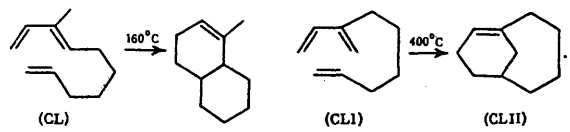
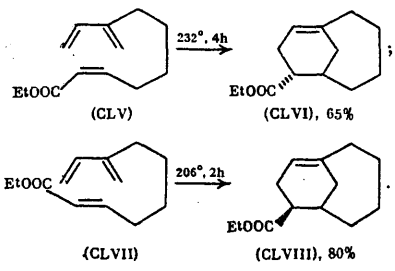


Table 3 shows that the two isomeric trienes *E*-(CLIII) and *Z*-(CLIV) give rise to the same bridged olefin. Kinetic studies have demonstrated that electron-accepting groups accelerate the reaction and that the latter proceeds *exo*-stereoselectively. The cyclisation of compounds *Z*-(CLV) and *E*-(CLVII), leading to the isomeric olefins (CLVI) and (CLVIII), is particularly interesting:

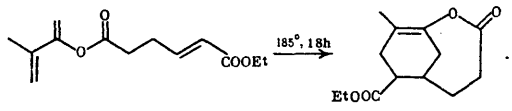



(CLV) (CLVI), 65%

(CLVII) (CLVIII), 80%

These isomers can be readily distinguished on the basis of physicochemical and spectroscopic data. The ratio $k_{(CLV)}/k_{(CLVII)} = 13$ (201 °C) shows that the secondary orbital interaction cannot determine the stereoselectivity of this type of IAMC[4 + 2].

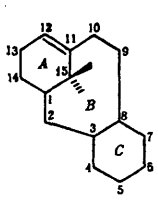
The IAMC[4 + 2] reaction of ethyl 1-methylene-2-methyl-(propenyl)hex-2-enedioate (CLIX), leading to the formation of the bridged enol lactone (CLX) in a high yield, has also been investigated: [87]



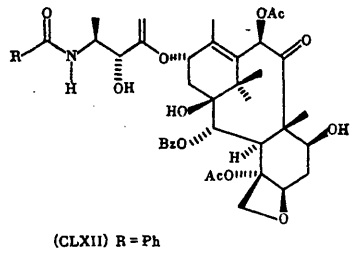

(CLIX) (CLX), 78%

### 3. The 6/<6-Annelated System

It is noteworthy that this system is rarely encountered; despite this, it has attracted the attention of organic chemists, since representatives of compounds of this class exhibit unique properties. For example, taxane diterpenes, isolated from certain *Taxus* species, contain the unusual tricyclic carbon skeleton (CLXI), in which the eight-membered *B* ring is sterically strained. [88] Taxol (CLXII) and cephalomannine (CLXIII) exhibit extremely high antileukaemic and antitumour activities.

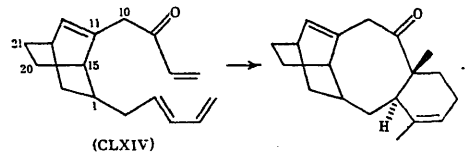


(CLXI)



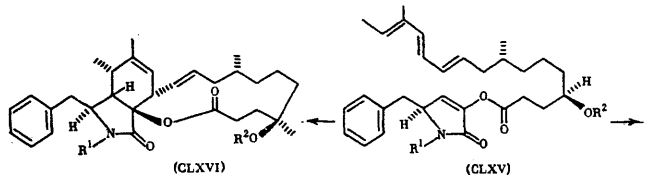
(CLXII) R = Ph
(CLXIII) R = —CMe=CHMe

Although the difficulty of effecting the closure of the *B* ring makes it difficult to obtain compounds of this kind, the IAMC[4 + 2] of the triene (CLXIV) takes place readily. The closure of the B ring is facilitated by the rigid disposition of the five carbon atoms C(2), C(1), C(15), C(11), and C(10), which is due to the fixed boat conformation of the *A* ring: [89]

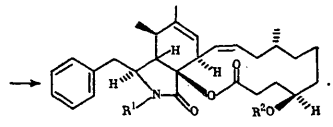


(CLXIV)

The formation of the macrocyclic lactam ring is one of the complex tasks in the synthesis of cytochalasin *B* and related compounds. [90] The above product has been successfully synthesised in the two stereoisomeric forms (CLXVI) and (CLXVII) by the application of a novel and simple procedure involving the IAMC[4 + 2] of the triene (CLXV): [91]



(CLXVI) (CLXV)

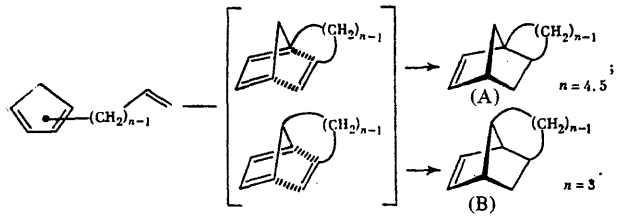


(CLXVII)

## IV. THE FORMATION OF BRIDGED CYCLIC SYSTEMS FROM ENDOCYCLIC DIENES

### 1. Cyclopenta-1,3-diene and Furan

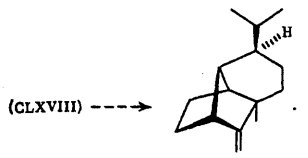
Experiments have shown that, depending on the length of the chain connecting the diene and the dienophile, the IAMC[4 + 2] of alkenylcyclopentadienes yields only two types of tricyclic adducts, (A) and (B), out of the possible twelve isomeric forms: [92,93]




It is remarkable that, when $n = 4$ or 5, then IAMC[4 + 2] leads specifically to a structure of type (A) [via the 1-(*n*-alkenyl)-isomer], while $n = 3$ affords exclusively tricyclo[4.3.0.0$^{3,7}$]non-4-ene [type (B)] via the 5-(*n*-alkenyl)-isomer.

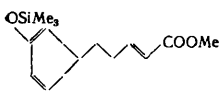
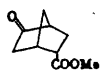
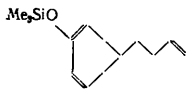
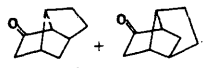
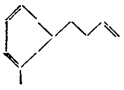
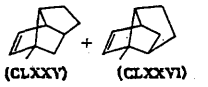
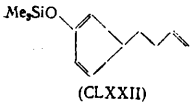
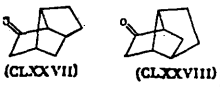
The IAMC[4 + 2] of certain alkenylcyclopentadienes has been carried out [94] (Table 4). The formation of only one regioisomer (CLXVIII) from the triene (CLXIX) is fully consistent with the prediction based on the frontier molecular orbital theory. [95] The cycloaddition of the trienes (CLXX), (CLXXI), and (CLXXII) is extremely important, since the unusual instance, where the formation of the products (CLXXIII), (CLXXV) and (CLXXVII) rules out the biradical cyclisation mechanism, is demonstrated here. [96] It is noteworthy that the precursors of compounds (CLXXIII),

(CLXXIV), (CLXXVI) and (CLXXVIII) are unstable and are converted into a stable form at the instant of their synthesis. The sesquiterpene tricyclic hydrocarbon (±)-sativene (CLXXIX) is readily and stereoselectively synthesised from compound (CLXVIII) in 32% yield: [97]




(CLXXIX)

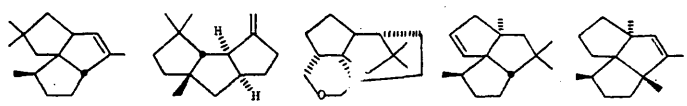
Table 4. Data for the IAMC[4 + 2] of the alkenylcyclopentadienes (CLXX), (CLXXI), (CLXXII), and (CLXIX). [94]

| Trienes | Conditions | Products | Yield, % |
|---|---|---|---|
|  (CLXIX) | 110°, 3 days |  (CLXVIII) 100 : 0 | 95 |
|  (CLXX) | 250°, 24 h |  (CLXXIII) (CLXXIV) 54 : 46 | 72 |
|  (CLXXI) | 250°, 24 h |  (CLXXV) (CLXXVI) 73 : 27 | 30 |
|  (CLXXII) | 250°, 24 h |  (CLXXVII) (CLXXVIII) 78 : 22 | 77 |

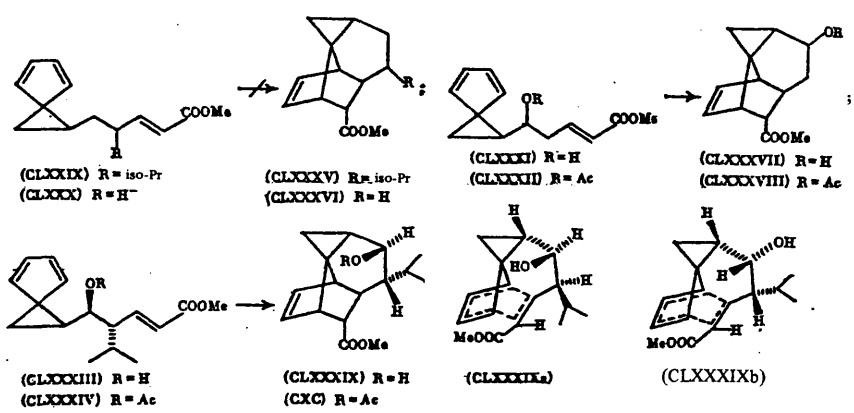
The influence of oxygen-containing substituents in the side chain on the reactivity in the IAMC[4 + 2] of the 5-(spiro-2,4-hepta-4,6-dien-1-yl)pent-2-enoates (CLXXIX)–(CLXXXIV) has been discussed in detail. [98]

The compounds obtained are intermediates in the synthesis of sesquiterpenes—sinularene, longifolene, sativene, etc. It was observed that the trienes (CLXXIX) and (CLXXX) do not cyclise in the course of 65 h at 195 °C, while the trienes (CLXXXI) and (CLXXXII) are converted into compounds (CLXXXVII) and (CLXXXVIII) in 60% yield after 6 h at 180 °C. It is of interest that the simultaneous employment of both substituents (OR and iso-Pr) in the side chain does not suppress the cyclisation under these conditions. It has been established that, in the presence of oxygen-containing substituents, the dienophile component of the triene is oriented relative to the plane of the cyclopentadiene ring in a way ensuring a position favouring cyclisation. This has been confirmed by the analysis of the $^1$H NMR spectra of the initial trienes: it was found that the signals of the β-hydrogen atoms in the dienophile component resonate about 5.0 p.p.m. instead of the usual range 6.5–7.5 p.p.m., which indicates the shielding of these atoms by the cyclopentadiene ring. This type of phenomenon has not been observed for the trienes (CLXXIX) and (CLXXX). In the cyclisation of the trienes (CLXXXIII) and (CLXXXIV), only one TS (CLXXXIXb) is actually produced of the two possible TS (CLXXXIXa) and (CLXXXIXb). The formation of one isomer can be accounted for by the unfavourable interactions between the isopropyl group and the *exo*-hydrogen atom in the TS (CLXXXIXa). However, the cause of the appearance of conformations suitable for IAMC[4 + 2] when oxygen-containing substituents in the C(5) position are used remains unknown.

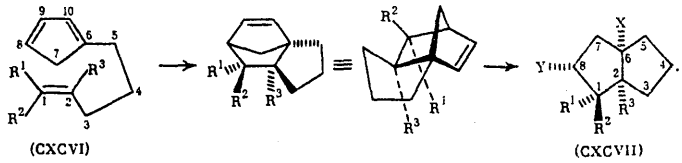
In order to synthesise polyquinane natural products, in particular pentalenene (CXCI), capnellene (CXCII), quadrone (CXCIII), silphinene (CXCIV), and isocomene (CXCV), a study has been made of the IAMC[4 + 2] reactions of several alkenylcyclopentadienes ($n$ = 4). [99]




The basic skeleton of these compounds, namely the bicyclo[3.3.0]octane ring (CXCVII), is readily produced by the cleavage of the double bond in the adducts obtained by the



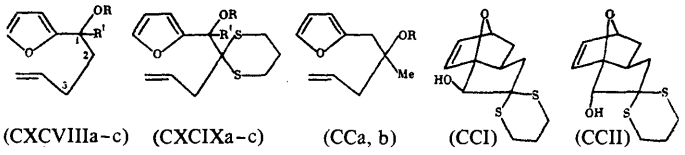
IAMC[4 + 2] of the trienes (CXCVI):



(CXCVI) (CXCVII)

It has been established that, under the conditions of the *trans*-disubstitution in the dienophile component, the reaction proceeds fairly readily and with a high yield of products. In each case two epimeric compounds are produced. Geminal substitution in the C(4) position in the side chain greatly accelerates the IAMC[4 + 2], which indicates the appearance of the TS conformation favourable for the interaction of the diene and dienophile components of the trienes. The stereochemistry of the adducts has been investigated using the nuclear Overhauser effect.

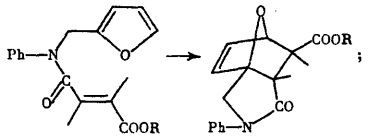
In contrast to alkenylcyclopentadienes, in the case of alkenylfurans the stereochemistry of the junction between the rings formed between the diene and ene fragments is more definite owing to the absence of 1,5-migration in the furane ring.[100] The influence of substituents and solvents on the IAMC[4 + 2] reaction where the α-substituted furan ring is used as the diene component has been investigated.[101] For this purpose, a study has been made of the cyclisation of compounds [CXCVIII, R = R′ = H (a); R = $PhCH_2$, R′ = H (b); R = H, R = Me (c)], [CXCIX, R = R′ = H (a); R = Bz, R′ = H (b); R = H, R′ = Me (c)], and [CC, R = $PhCH_2$ (a); R′ = H (b)]:



(CXCVIIIa-c) (CXCIXa-c) (CCa, b) (CCI) (CCII)

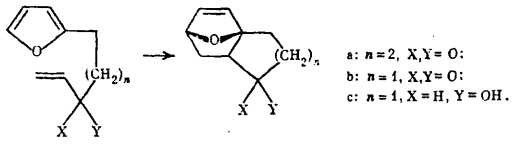
It has been shown that the trienes (CXCVIIIa-c), which have no substituents at the C(1) atom in the side chain, do not undergo the IAMC[4 + 2] reaction. Thermolysis of the trienes takes place *exo*-stereoselectively. The mixture of the (CCa) epimers used gives rise to only traces of the four isomeric reaction products. The triene (CCb) proved to be unreactive under these conditions. The presence of the dithian ring at the C(2) atom in the side chain of compound (CXCIXa) promotes the successful occurrence of the reaction, as a result of which one obtains a mixture of the epimers (CCI) and (CCII) in 63% yield. Geminal substituents at the C(1) atom greatly influence the yield and rate of reaction; thus the presence of the Me and OH geminal groups in the triene (CXCIXc) appreciably accelerates the rate of reaction, while the replacement of the OH group by the ester group in compound (CXCIXb) retards the cyclisation compared with the triene (CXCIXa). The low yield of products in the cyclisation in water compared with the reaction in other solvents can be accounted for by micelle formation. Thus the rate of reaction and the yield of products obtained from α-alkenylfurans greatly depend on the nature of the substituents in the bridging carbon chain; a correct choice of substituents makes it possible to obtain a five-membered carbon ring with a high yield.

The kinetics of the cyclisation of the triene (CCIII) has been investigated spectroscopically;[29] the activation parameters found ($E_A^{\neq}$ = 72.5 kJ $mol^{-1}$, $\Delta H^{\neq}$ = 69.8 kJ $mol^{-1}$, $\Delta S^{\neq}$ = −62 J $mol^{-1}$ $K^{-1}$, and $\Delta V^{\neq}$ = −25 $cm^3$ $mol^{-1}$) show that the bulk of the TS in the IAMC[4 + 2] diminishes with increase of pressure to a lesser extent than in the case of IRMC[4 + 2].



(CCIII)
R = H, Et.

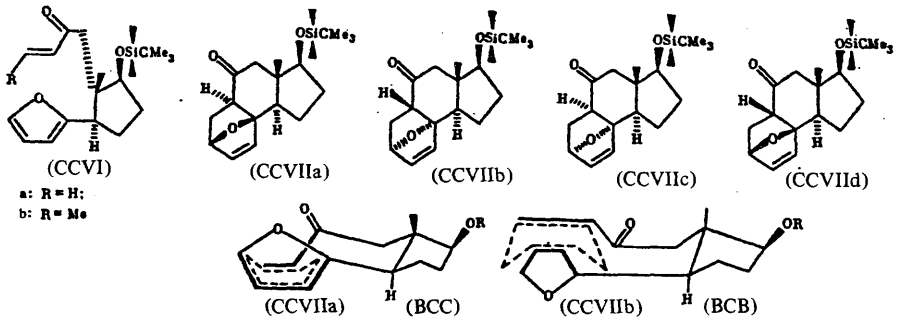
The IAMC[4 + 2] reaction of the trienes (CCIVa–c) has been used to develop a new method of synthesis of corticosteroids and certain characteristic features of this cyclisation have been discovered:[102,103]



a: n = 2, X,Y = O;
b: n = 1, X,Y = O;
c: n = 1, X = H, Y = OH.

(CCIVa-c) (CCVa-c)

A series of model experiments established that, in order to construct the simple oxatricyclo[$6.2.1.0^{1,6}$]undecene system (CCVa, n = 2), it is essential to activate the dienophile in the triene (CCIVa). Indeed the ketone (CCIVa) is readily converted into the corresponding *exo*-adduct (CCVa), while the replacement of the C=O group by OH in the initial triene prevents the IAMC[4 + 2]:



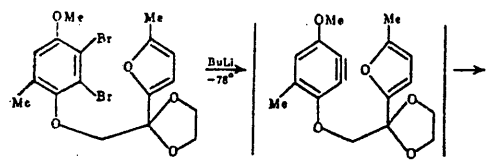
(CCVI)
a: R = H;
b: R = Me

(CCVIIa) (CCVIIb) (CCVIIc) (CCVIId)

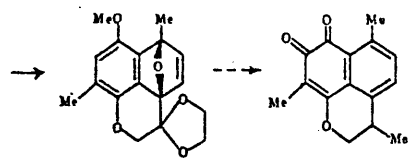
(CCVIIa) (BCC) (CCVIIb) (BCB)

Only the products (CCVIIa) and (CCVIIb) are formed in proportions of 1:8 and in an overall yield of 61% in the thermolysis of compound (CCVIa) out of the four possible isomers (CCVIIa–d). Under these conditions, the methyl-substituted triene (CCVIb) does not react. The formation of only the *exo*-adducts (CCVIIa) and (CCVIIb) in this reaction is not surprising, since the structures of the adducts (CCVIIc) and (CCVIId) are more distorted.[104] It is of interest that at low temperatures the adduct (CCVIIb) is formed preferentially. Investigation revealed that the TS from which the product (CCVIIa) is obtained has the boat-chair-chair (BCC) conformation. Calculation of the force field showed that the boat-chair-boat (BCB) conformation is preferable in cyclododecane, which suggests that the TS for the reaction has the preferred BCB conformation.

Mansonone-E (CCX) isolated from the wood of *Mansonia altissima*, which is an *o*-naphthoquinone widely distributed in nature, can be smoothly synthesised from compound (CCVIII);[105] the key stage in the synthesis is the IAMC[4 + 2] of the intermediate triene (CCIX) containing the furan and benzene fragments:

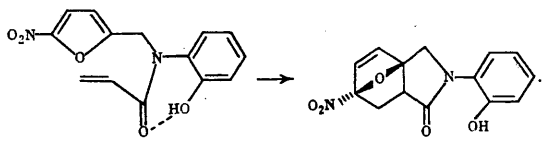



(CCVIII) (CCIX)




(CCX)

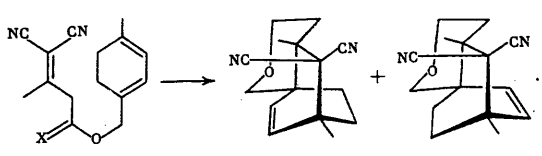
The IAMC[4 + 2] of the triene (CCXI) affords the product (CCXII) in a satisfactory yield,[106] the stereospecificity of the reaction being determined by the intramolecular hydrogen bond between the amide C=O group and the phenolic hydroxyl:




(CCXI) (CCXII)

## 2. Cyclohexa-1,3-diene

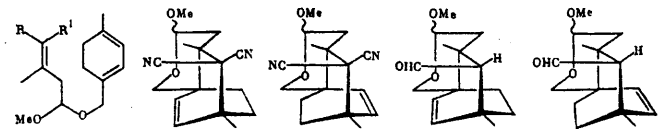
Alkenylcyclohexa-1,3-dienes also enter smoothly into the IAMC[4 + 2] reaction. It has been established that the triene (CCXIII, X = $H_2$) readily gives rise to the cyclisation products (CCXIV) and (CCXV) in proportions of 2.2:1:[107]




(CCXIII) (CCIV) (CCV)

However, its nearest homologue (CCXIII, X = O) does not cyclise under these conditions but polymerises.

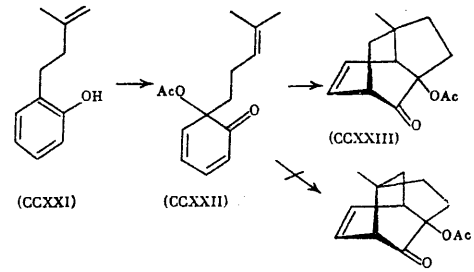
The thermolysis of the triene (CCXVIa) at 210 °C in the course of 22 h produces smoothly a mixture of the cyclic products (CCXVII) and (CCXVIII) in proportions of 1.8:1 in 80% yield. It is of interest that in both cases the axial disposition of the OMe group is preferred (*a*:*e* = 2.75:1). Cyclisation is possible also in the presence of only one electron-accepting group. For example, the IAMC[4 + 2] of the *E*-aldehydoacetal (CCXVIb) affords the products (CCXIX) and (CCXX) in proportions of 12.8:1 (*a*:*e* = 1:1 in both cases). The desired product is not formed in the IAMC[4 + 2] of the corresponding *E*-ester (CCXVIc); instead methanol is eliminated from the acetal and an inactive tetraene is therefore generated:




(CCXVI) (CCXVII) (CCXVIII) (CCXIX) (CCXX)

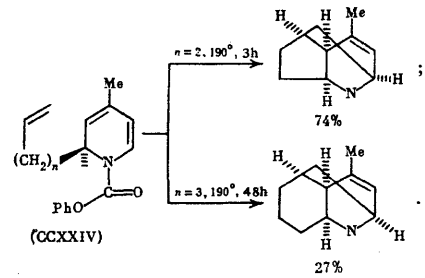
a: R = $R^1$ = CN;
b: R = CHO, $R^1$ = H;
c: R = COOEt, $R^1$ = H

Vessely oxidation of *o*-isopentenylphenol (CCXXI) by $Pb(OAc)_4$ in acetic acid gives rise to the substituted cyclohexa-2,4-dienone (CCXXII), which is converted into isotwist-8-en-2-one (CCXXIII), without isolation, on heating in boiling xylene:[108]




(CCXXI) (CCXXII) (CCXXIII)

The IAMC[4 + 2] reaction of the dihydropyridines (CCXXIV) has been used to synthesise the various *cis*-decahydroquinoline alkaloids such as gephyrotoxin:[109]



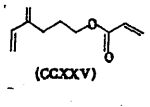
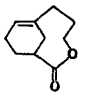
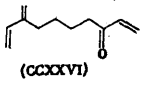
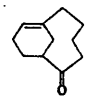
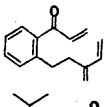
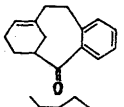
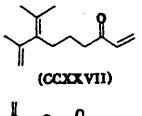
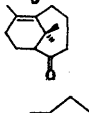
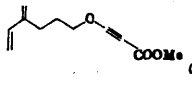
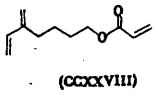
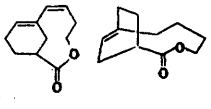

(CCXXIV)

## V. CATALYTIC INTRAMOLECULAR [4 + 2]CYCLOADDITION

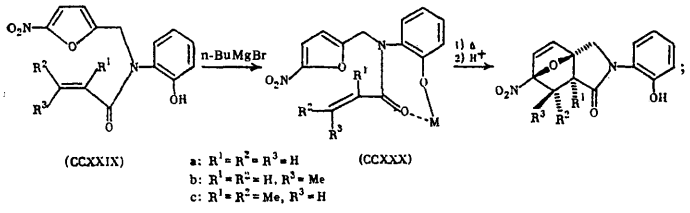
Lewis acids have been used as catalysts in order to increase the rate of pericyclic reactions.[110,111] The catalytic effect of Lewis acids is effectively manifested also in intramolecular Diels–Alder reactions, where fairly severe conditions are required in many instances to achieve regio- and stereo-specificity.[112] For example, the IAMC[4 + 2] of compounds in which the dienophile component is attached to the diene component in the 2-position, leading to the formation of strained bridged cycloalkenes, requires a high temperature.[15] Various Lewis acids have been used in the IAMC[4 + 2] reaction of 4-methylenehex-5-enyl acrylate

(CCXXV). This triene undergoes thermal cyclisation at 139 °C ($\tau_{1/2}$ = 1.8 h). The complex formed between the triene and the Lewis acid is $10^4$ times more reactive than the triene itself; this is comparable with the increase of the rate of the IRMC[4 + 2] catalysed by Lewis acids ($10^5$ at 21 °C).[113] The rate of the catalytic reaction of the triene (CCXXV) is slightly influenced by the polarity of solvents; on passing from pentanes to methylene chlorides, the rate changes only slightly ($k_{CH_2Cl_2}/k_{C_5H_{12}}$ = 2.8). Table 5 presents data on the catalytic IAMC[4 + 2] of certain trienes. It is of interest that the methylated trienone (CCXXVII) is much more reactive than the non-methylated homologue (CCXXVI) under catalytic conditions. This finding conflicts with the result of thermal cyclisation, where the trienone (CCXXVI) is more reactive than compound (CCXXVII). A high reactivity is manifested by dienes when electron-accepting dienophiles are employed in catalytic processes.[114] However, Lewis acids influence only insignificantly the regioselectivity of the IAMC[4 + 2] reaction.[115] The thermal cyclisation of the triene (CCXXVIII) (180 °C, 12 h) affords a mixture of the 1,3- and 1,4-adducts in proportions of 10:1. In the presence of $Et_2AlCl$ (1 equivalent), the cyclisation is completed after 1 h at 21 °C with formation of the same products in proportions of 81:19. The slight change of regioselectivity in favour of the 1,4-isomer agrees with the predictions of the frontier molecular orbital theory.[116] It has also been discovered that the regioselectivity of the IAMC[4 + 2] reaction depends little on temperature.

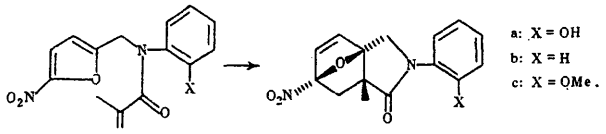
Table 5. Data for the catalytic IAMC[4 + 2] of certain trienes.[112]

| Trienes | Products | Conditions | Yield, % |
|---|---|---|---|
|  (CCXXV) |  | 21°, 4 h | 85 |
|  (CCXXVI) |  | 21°, 2 h | 75 |
|  |  | 21°, 1 h | 71 |
|  (CCXXVII) |  | 21°, 5 min | 70 |
|  |  | 21°, 12 h | 85 |
|  (CCXXVIII) |  | 21°, 1 h | 90 |

As a result of its aromaticity, furan is a relatively unreactive diene and the IRMC[4 + 2] reaction of nitrofuran with electron-accepting dienophiles should be even more difficult.[114] Despite such an unfavourable combination of the diene and dienophile, the IAMC[4 + 2] of the trienes (CCXXIX) can be achieved readily after treatment with butylmagnesium bromide:[117]

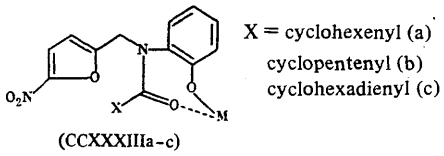



The formation of the complex (CCXXX) as a result of the intramolecular coordination between the phenoxide and amide groups leads to the mutual approach of the diene and dienophile fragments, favouring cyclisation. Subsequently this reaction was investigated in the absence of Grignard reagents, the substituent in the benzene ring being varied:




(CCXXXIa-c) (CCXXXIIa-c)

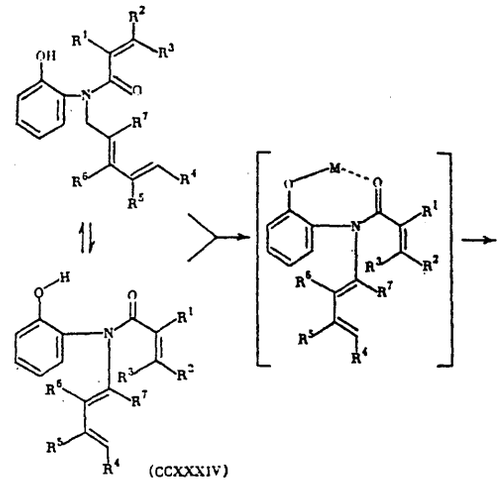
After 7 h in benzene, the product (CCXXIIa) is obtained in 75% yield, while the yields of the products (CCXXXIIb) and (CCXXXIIc) are only 30 and 11% respectively. The shift of the absorption by the C=O group in the IR spectrum confirmed the presence of an intramolecular hydrogen bond between the hydroxyl proton and the C=O group in the initial compound (CCXXXIa), which leads to the coplanarity of the dienophile part of the molecule and hence to an increase of the reaction rate. The solvation effects have only a slight influence on the yield and rate of the cyclisation reaction. One of the main factors determining the course of the cycloaddition is the steric hindrance in the dienophile component of the triene.



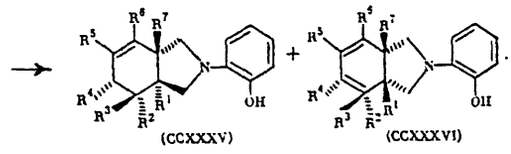

(CCXXXIIIa-c)

Examination of molecular models shows that the axial proton in the cyclohexene ring of cyclohexene-1-carboxamide (CCXXXIIIa) hinders the approach of the cyclohexene ring to the furan ring, which has not been observed for the trienes (CCXXXIIIb) and (CCXXXIIIc). It has been shown that molybdenum and tungsten complexes of the type $[MCl(CO)_2(\eta^3\text{-allyl})(NCMe)_2]$ appreciably accelerate this reaction.[118] The steric structures of the products have been established by NMR using the nuclear Overhauser effect; the *exo*-configuration with the *anti*-position of the Me group relative to its bridging oxygen atom has been attributed to them.

The IAMC[4 + 2] reaction between acyclic diene and αβ-unsaturated amide fragments has been thoroughly investigated[118,120] using intramolecular coordination with participation of metal salts:

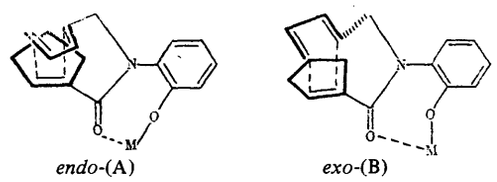


(CCXXXIV)



(CCXXXV) (CCXXXVI)

When magnesium salts are used, the IAMC[4 + 2] of *N*-(*trans*,*trans*-alka-2,4-dienyl)-*N*-(2-hydroxyphenyl)acrylamide derivatives (CCXXXIV) is greatly accelerated and the corresponding products (CCXXXV) and (CCXXXVI) are obtained in high yields; the *exo* : *endo* isomer ratio is approximately 3 : 2. The analogous reaction with *N*-(*trans*,*trans*-alka-2,4-dienyl)-*N*-(2-hydroxyphenyl)cyclopentene-1-carboxamide results in the preferential formation (from 60 : 40 to 85 : 15) of *trans*-joined *exo*-products in a satisfactory yield. The addition of 4-t-butylcatechol in catalytic amounts to the reaction mixture inhibits the polymerisation process. The preferential formation of the *exo*-products is not surprising because, on coordination of phenol to the magnesium salts, the coordination of magnesium to the oxygen of the C=O group makes the molecular conformation more rigid and the TS (A) in the *endo*-cyclisation becomes more strained than the *exo*-TS (B):

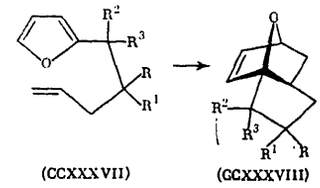


*endo*-(A) *exo*-(B)

When strong Lewis acids such as aluminium or tin salts are used, a balance between the steric control and control by secondary orbital interaction is observed, so that two products are obtained in almost identical amounts, as in the non-catalytic reaction.

It has been shown[40,41] that the thermal cyclisation of methyl deca-2,7(*E*),9-trienoates (XXXIII)–(XXXV) produces the preferentially *trans*-joined hexahydroindenes (XXXVIIa)–(XL) (Table 2). The catalytic cyclisation of the *trans*-decatrienoates (XXXIII) and (XXXV) using Lewis acids such as $AlCl_3$, $EtAlCl_2$, $Et_2AlCl$, $BF_3.Et_2O$, etc. proceeds fully stereospecifically with formation of *trans*-joined products.[115] However, this procedure is not feasible for *cis*-decatrienoates, i.e. the stereoselectivity of the catalytic cyclisation of these compounds hardly differs from that of the thermal cyclisation. The lack of a change in the stereoselectivity of the cyclisation of the trienes (XXXIV) and (XXXVI) can be explained by the fact that the enhancement of the secondary orbital interaction between the ester carbonyl group and the Lewis acid is insufficient to overcome the hindrance to the formation of the *trans*-TS.

The thermal cyclisation of the methyl esters of the (*E*,*E*,*E*)- and (*Z*,*E*,*E*)-12-methyltrideca-2,8,10-trienoic acids (CIII) and (CIV) proceeds non-stereospecifically with formation of 50 : 50 mixtures of *cis*- and *trans*-joined products. In the presence of Lewis acids ($Et_2AlCl$), the stereoselectivity and the yield of products changed to a significant extent.[68] The acid-catalysed cyclisation proceeds mainly with formation of *endo*-products, since the stereocontrol of the reaction is due to the secondary orbital interaction. β-Cyclodextrin has been used successfully as the catalyst in the IAMC[4 + 2] of 1-(2-furyl)-1-hydroxy-2-R,2-R′-pent-4-ene (CCXXXVII) which resulted in the formation of a mixture of the products (CCXXXVIIIa) and (CCXXXIIIb) in an overall yield of 91%:[121]



(CCXXXVII) (GCXXXVIII)

a: $RR^1 = S(CH_2)_3$, $R^2 = H$, $R^3 = OH$
b: $RR^1 = S(CH_2)_3$, $R^2 = OH$, $R^3 = H$.

Thus the data published in recent years permit the conclusion that IAMC[4 + 2] is of enormous interest and we hope that further development of this unique field of chemistry will lead to extensive possibilities for the specific synthesis of the most important natural products and their analogues.

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During the preparation of the manuscript for the press, a fairly large number of publications devoted to IAMC[4 + 2] appeared.[122–207] One of these is a review[122] which deals with the latest advances in the intramolecular Diels–Alder reaction and its application to the synthesis of complex natural products. In particular the synthesis of the bicyclo[4.3.0]nonene, bicyclo[4.4.0]decene, and bicyclo-[5.4.0]undecene systems and bridged bicyclo[*n*.3.1]alkenes is discussed. In contrast to the above review,[122] in the present review attention has been concentrated on the discussion of the synthesis of products from the corresponding trienes and on catalytic IAMC[4 + 2].

The main trend in other investigations[123–207] involved the study of the stereo- and regio-selectivities of IAMC[4 + 2] for the construction of the basic skeletons of natural products using various synthetic procedures, in particular catalysts of various type, an activated double bond, bulky substituents at chiral centres, etc.

The vigorous growth of the number of publications on the IAMC[4 + 2] reaction during such a brief period (1984–1985) again indicates the timely and promising nature of this branch of organic chemistry.

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# The Mechanism of the Reaction of C-Nitroso-compounds with Alkenes

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Published data on the study of the chemical aspects of the reaction of C-nitroso-compounds with alkenes have been examined and critically reviewed. The multi-stage nature of the process has been emphasised. The dependence of the mechanisms of the primary stage and subsequent stages of the reaction on the structure of the reagents and the reaction conditions has been discussed. An attempt has been made to explain the contradictory data on the structure of the final reaction products in terms of the variety of possible directions for the transformation of the intermediates. The characteristics of the chemical reaction of C-nitroso-compounds with diene polymers have been examined.
The bibliography contains 117 references.

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## I. INTRODUCTION

The considerable practical importance acquired in recent years by C-nitroso-compounds, which have found application as rubber modifiers and stabilisers both at the polymer formation stage[1-5] and in its conversion to finished rubber articles,[6-12] has led to increased interest in the study of the chemical aspects of the reaction of an unsaturated hydrocarbon chain with C-nitroso-compounds.

However, in spite of the fact that a fairly large number of published papers have been devoted to the mechanism of the reaction of C-nitroso-compounds with alkenes, this extensive but extremely contradictory experimental material has not been reviewed (apart from a brief review[13] dealing only with the reactions of C-nitroso-arenes and covering the literature up to 1970). In the present work an attempt is made to fill this gap.

Most workers who have studied the reaction of C-nitroso-compounds with monoalkenes point out that it is a multistage process, but there is lack of agreement on its basic parameters: the stoichiometry, the reaction centre in the alkene molecule, the nature of the primary attack on the alkene by the nitroso-compound and the intermediate stages, and the structures of the final products. Thus depending on the structure of the reagents and the conditions of the process, the following nitrogen-containing final reaction products have been isolated and identified: alkenylaryl- or alkenylalkyl-hydroxylamines, nitrones, azoxybenzenes, secondary and primary amines, azomethines, oxazetidines, oxadiazoles, isoxazolines, and oxime ethers.

The following main mechanisms have been proposed for the first stage of the reaction of nitroso-compounds with alkenes: 1) "Diels–Alder pseudo-condensation" ene synthesis with the formation of a tertiary hydroxylamine and prototropic displacement of the double bond; some authors assume intermediate 1,2 cyclo-addition with the formation of an oxazetidine; 2) direct radical allyl condensation with the transfer of an allyl proton to the NO group and the formation of a hydroxylamine derivative; 3) the formation of a 2:1 molecular adduct of the nitroso-compound and the alkene as a substituted oxadiazole; 4) a homolytic process involving direct electron transfer from the C=C bond to the NO bond with the formation of nitroxide radicals; 5) the formation of a charge-transfer complex from the alkene and the nitroso-compound and its decomposition via a radical–ion stage.

The products obtained in the first stage undergo further heterolytic and homolytic transformations to give the final products indicated above.

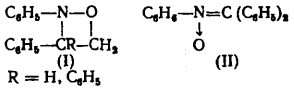
To introduce greater order into the often confused and contradictory published data, the present review is restricted to the study of the reactions of C-nitroso-compounds with alkenes with and without an allyllic hydrogen atom.

The present review examines the reactions of both aromatic and stable aliphatic nitroso-compounds, such as nitrosotrihalogenomethanes and nitroso-t-butane, which although differing in many of their characteristics (spectral,[14] polarographic,[15] etc.), are similar in their chemical properties, in particular in their reactions with alkenes.

## II. REACTIONS OF C-NITROSO-COMPOUNDS WITH ALKENES NOT CONTAINING γ-PROTONS

This group of alkenes includes styrene, stilbene, 1,1-diphenylethylene, and their fluorinated analogues, but particular attention has been paid to the reactions of styrene. This interest in styrene is understandable, since aromatic nitroso-compounds are excellent inhibitors of free-radical reactions, and in the study of the processes of radical polymerisation and copolymerisation of styrene, which have found industrial application, it is important to investigate not only the stage involving the termination of the growing polymer chain but also the direct reaction of the inhibitor with the monomer.

In an early paper,[16] the adducts of styrene and 1,1-diphenylethylene with nitrosobenzene were assigned the oxazetidine structure (I).

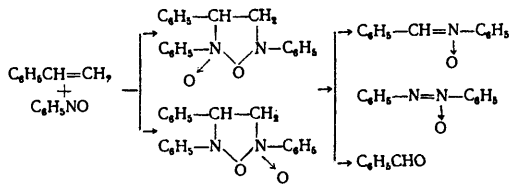


(I) R = H, $C_6H_5$ (II)

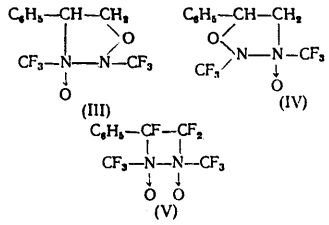
This view was criticised even at the time, however. According to Ref.17, the product of the reaction of nitrosobenzene with 1,1-diphenylethylene has the nitrone structure (II).

Hepfinger[18] considers that the products of the reaction of nitrosobenzene with styrene are unstable isomeric oxadiazole N-oxides, which decompose to give the α,N-diphenylnitrone,

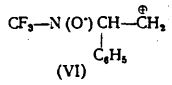
azoxybenzene, and benzaldehyde:



At the same time, one of a cycle of studies of the reaction of trifluoronitrosomethane with alkenes[19] showed that, depending on the reaction temperature, the products may be adducts of this nitroso-compound with styrene and trifluorostyrene in the ratio 2:1 (<−70 °C) and 1:1 (>−70 °C); the 1:1 adduct was assigned the oxazetidine structure (I), and the 2:1 adducts the structures (III) and (IV) for styrene, and (V) for trifluorostyrene:



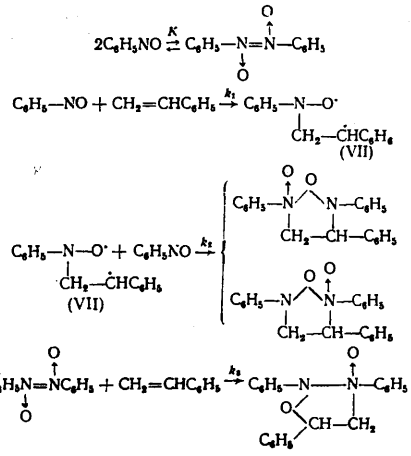
According to Ref.20, the first stage of the process gives a donor–acceptor complex, whose transformations are determined by the structure of the alkene. Paramagnetic intermediate species were detected, and in the case of the reaction of trifluoronitrosomethane with styrene they were assigned the radical–cation structure (VI):



Nitroxide radicals are also formed in the reaction with trifluorostyrene.[21]

The authors cited, however, do not suggest a mechanism which could explain the formation of the cyclic products (III)–(V).

Developing the ideas of Refs.18 and 19, a group of Japanese workers,[22] who studied the reactivity and kinetics of the reaction of nitrosobenzene with styrene, and also the reaction of the corresponding substituted derivatives, proposed the following scheme for the process:



They consider that the data they obtained on the kinetics of the reaction (order of the reaction with respect to nitrosobenzene between 1 and 2; its dependence on the initial concentration of the reagents—an increase with increase in concentration while preserving first order with respect to styrene) confirm the proposed mechanism, since in dilute solutions, the nitroso-compounds, which tend to dimerise,[23] are present chiefly in the monomeric form.

A study of the reactivity of substituted nitrosobenzenes showed that the presence of electron-donor substituents in the *p*-position decreases the reaction rate, whereas the presence of electron-acceptor substituents increases the reaction rate; a linear relationship was obtained between the reaction rate constants for the substituted nitrosobenzenes and the Hammett constants of the substituents for electrophilic reactions $\sigma^{\oplus}$, in good agreement with the view that the double bond in the styrene molecule is nucleophilic.

Among substituted styrenes, α-methylstyrene is much more reactive than β-methylstyrene; this is attributed not only to the more nucleophilic character of the double bond in the α-isomer and the stabilisation of the intermediate biradical (VII) but also to steric hindrance in the β-methylstyrene molecule.

The possible reaction of styrene with various derivatives of nitrosobenzene in the dimeric form has been noted.[24] The reaction is of second order with respect to the nitroso-compound, and paramagnetic species are formed in the reaction.

Thus although different workers have different views on the nature of the reaction of nitroso-derivatives with unsaturated hydrocarbons not containing γ-protons, most believe that cyclic products of the addition of the nitroso-compounds to the double bond are formed. Paramagnetic species are produced in the reaction. Benzylidene-N-phenylnitrone, azoxybenzene, and benzaldehyde have been separated from the decomposition products of the cyclic adducts of nitrosobenzene with styrene.

Some authors[25] have studied a series of alkenes without distinguishing between those which contain an allyl hydrogen atom and those which do not, and have examined their reactions with nitroso-compounds from the same viewpoint. The data given below, however, show that the presence or absence of γ-protons in the alkene has a significant influence on the mechanism of the process.

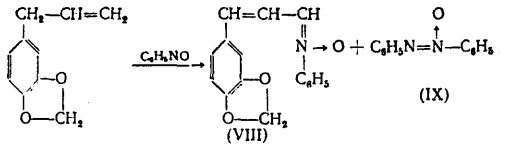
## III. THE REACTION OF C-NITROSO-COMPOUNDS WITH ALKENES CONTAINING AN ALLYL HYDROGEN ATOM

Before reviewing studies devoted directly to the mechanism of the reactions of nitroso-compounds with alkenes containing primary, secondary, or tertiary hydrogen atoms in the allyl position, the structure of the final products of this reaction can be considered.

### 1. Structure of the Final Products

A critical review of published data on the products of the reactions of C-nitroso-compounds with alkenes containing an allyl hydrogen atom is difficult, since on the one hand, workers studying these processes encounter objective difficulties in identifying the final products, because of their tendency to undergo interconversion, and, on the other hand, some authors try to transfer experimental data relating to alkenes and nitroso-compounds with particular structures to other compounds of these classes. In the examination of the experimental material on the structure of the final products, therefore, specific reference will be made to the reagents for which the various regularities have been established.

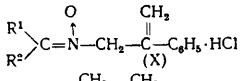
The reaction of C-nitroso-compounds with alkenes (safrole and various others) was first reported in Ref.26; the authors considered that the chief products of the reaction of nitrosobenzene with safrole are the nitrone (VIII) and azoxybenzene (IX).



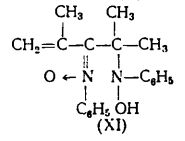
(VIII) (IX)

It was later shown[27] that azoxy-derivatives are formed in the reactions of *p*-nitro- and *p*-bromo-substituted nitrosobenzenes with cyclopentene, cyclohexene, propene, isobutylene, but-1-ene, *cis*- and *trans*-but-2-enes, and stilbene, the reaction taking from several seconds to several days, depending on the structure of the starting materials. The complete conversion of the nitrosobenzene into the azoxybenzene requires at least an equimolar quantity of the alkene. An appreciable quantity of azoxybenzene was isolated in the reaction of nitrosobenzene with 2-methylpent-2-ene.[28] The formation of nitrones in the processes studied was not reported.[27,28]

On the other hand, nitrones were identified as products of the reaction of α-methylstyrene and other alkenes containing an allyl hydrogen atom with chloronitrosoadamantane and other α-chloronitroso-compounds, where the nitrones were isolated as the hydrochlorides (X),[29] and also as products of the reaction of nitrosobenzene with tetramethylallene (in this case the bifunctional product (XI) with nitrone and hydroxylamine groups is formed).[30] In the last case, azoxybenzene was also isolated, but only as the product of the high-temperature treatment of compound (XI).

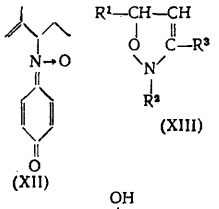


(X)

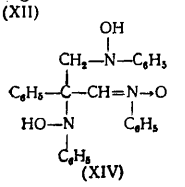


(XI)

When examining the possible separation of α-alkenylnitrones in the reactions of nitroso-compounds with alkenes, it must be borne in mind[31] that they are stable only when they have a structure capable of undergoing tautomerisation to give more stable forms (for example, the alkenylquinonimine oxide (XII), isomeric with the expected nitrone, is obtained from nitrosophenol and 2-methylpent-2-ene)[31,32] or have a high degree of resonance stability (the nitrone (VIII), isolated in the reaction of nitrosobenzene with safrole).



(XII) (XIII)

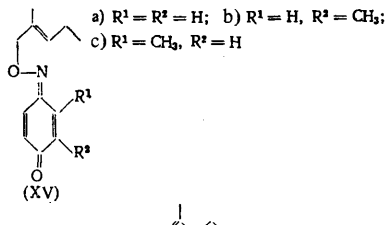


(XIV)

Unstable α-alkenyl-N-arylnitrones may undergo intramolecular cyclisation or react further with the alkene and the unreacted nitroso-compound.[33-38] These reactions naturally also take place with comparatively stable nitrones, but under more severe conditions; for example, the isoxazoline ring (XIII) is formed by intramolecular cyclisation.

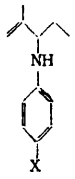
The instability of the products of the reactions of nitroso-compounds with alkenes is confirmed by the data of Ref.39. The author cited considers that at low temperatures (-10 °C), nitrosobenzene reacts with α-methylstyrene to form the 3:1 adduct α-[1-phenyl-1,2-di(N-phenylhydroxylamino)ethyl]-N-phenylnitrone (XIV), which subsequently at room temperature loses one N-phenylhydroxylamine fragment to form the cyclic 2:1 adduct, a substituted isoxazoline. Another example is the thermal rearrangement of alkenylquinonimine N-oxides (XII), formed as indicated above by the reactions of nitrosophenols with 2-methylpent-2-ene, to give O-alkenyl quinonimine oxime ethers (XV).[32] This rearrangement, which is analogous to the familiar thermal rearrangement of allylamine oxides into O-alkenylhydroxylamines[40-42] and of nitrones into O-alkenyl oxime ethers,[43,44] takes place only at comparatively high temperatures (100–120 °C) so that oxime ethers were found in appreciable quantities only in the products of the reaction of nitrosocresols with 2-methylpent-2-ene, which requires high temperatures.

The main products isolated[13,31,45] in the reaction of 2-methylpent-2-ene with *p*-nitrosophenol and N,N-dimethyl-*p*-nitrosoaniline are the corresponding *p*-substituted alkenylanilines (XVI).



a) $R^1 = R^2 = H$; b) $R^1 = H$, $R^2 = CH_3$; c) $R^1 = CH_3$, $R^2 = H$

(XV)



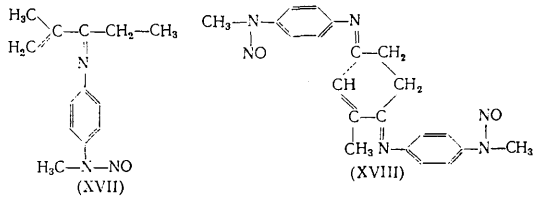
(XVI): X = OH, $N(CH_3)_2$

A characteristic feature of the reaction conditions in Ref.31 is a 12-fold excess of the alkene. In this case, in addition to the *p*-substituted N-alkenylanilines, the authors cited isolated a large number of resinous products, which they believed to be condensed nitrone structures. A small quantity of azoxybenzenes, azobenzenes, and primary *p*-substituted anilines, products of side reactions, was also obtained.

The comparative simplicity of the single-stage synthesis of N-alkenyl-*p*-phenylenediamines—a new class of effective antioxidants—by the reaction of N-substituted *p*-nitrosoanilines with alkenes[46] makes this process fully competitive with the industrial method for the production of familiar antioxidants with a similar structure, namely N-alkyl-*p*-phenylenediamines, which are usually obtained by hydrogenating nitroso-compounds followed by reductive alkylation of the anilines with ketones.[47]

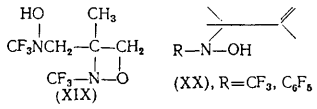
Another possible final structure is indicated in Ref.48, where the products of the reaction of N-methyl-N,4-dinitrosoaniline with alkenes are assigned the anil structure; the reaction with 2-methylpent-2-ene gives the 1:1 adduct (XVII), and the reaction with methylcyclohexane gives the 2:1 adduct (XVIII). The authors of Ref.13 consider, however, that the data given in Ref.48, on the basis of which the functional group in the final products (XVII) and (XVIII) was identified

as the azomethine group, can equally be related to an azomethine oxide (nitrone).



(XVII) (XVIII)

The cyclic products of the reaction of nitroso-compounds with alkenes not containing γ-protons, which are apparently the main final products or intermediate products in the case of allyl alkenes, have been reported to contain not only cyclised nitrones but also oxazetidines[49-51] or compounds containing hydroxylamine and oxazetidine groups.[51] Thus in the opinion of the authors of Ref.51, the 2:1 adduct of trifluoronitrosomethane and isobutylene has the structure (XIX).



(XIX) (XX), R=$CF_3$, $C_6F_5$

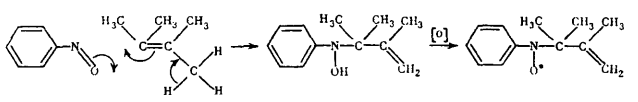
Some authors[25,51,52] consider that the final products of the reactions of alkenes with fluorinated nitroso-compounds are alkenylaryl- or alkenylalkylhydroxylamines (XX). Most workers, however, believe that substituted hydroxylamines are only intermediate compounds, and undergo further transformations, discussed below.

Analysis of published data on the structure of the final products of the reactions of nitroso-compounds with alkenes containing allyl hydrogen leads to the following conclusions: 1) in a large excess of the alkene, the reaction apparently takes place mainly to give the secondary amine and the nitrone or its transformation products; 2) in the absence of an excess of the alkene, appreciable quantities of azoxy-derivatives are found in the reaction products; 3) for perfluorinated nitroso-compounds, the formation of compounds with hydroxylamine or oxazetidine groups as final products is possible.

## 2. Mechanism of the Primary Stage of the Reaction

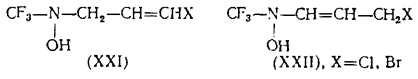
Most workers who have studied the reactions of C-nitroso-compounds with alkenes containing γ-protons consider that the initial stage is the ene addition of the nitroso-compound to give an unsaturated hydroxylamine. However, since these hydroxylamines are unstable and can be isolated and identified only in rare cases, there are other ideas regarding the primary stage.

The possibility of an ene reaction between a nitroso-compound and an alkene containing hydrogen on the α-methylene carbon atom was first reported in 1965.[53] Data were soon published[28] on the formation of a stable alkenyl aryl nitroxide radical, obtained by oxidising an extremely reactive alkenylarylhydroxylamine—an adduct of nitrosobenzene or some of its *o*-, *m*-, and *p*-derivatives with tetramethylethylene, chosen as an alkene whose symmetry makes it possible to obtain a resolved triplet in the EPR spectrum of the reaction product. The intermediate unstable alkenylarylhydroxylamine could not be isolated, and its formation was proved indirectly.



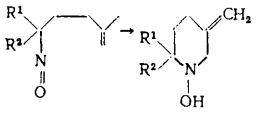
The possibility of ene synthesis with subsequent oxidation of the alkenylhydroxylamine to a nitroxide radical was confirmed in Ref.25, where the ene adduct of pentafluoronitrobenzene and tetramethylethylene was isolated in quantitative yield. Trifluoronitrosobenzene reacts similarly with an alkene. Many other authors also regard ene synthesis as the initial stage of the reactions of nitroso-compounds with alkenes.[20,46,52,54,55] The study of the reactivity of alkenes with different structures in the ene reaction is of considerable interest. The reactivity of butenes towards trifluoronitrosomethane decreases in the following order:[55] *cis*-$CH_3$–CH=CH–$CH_3$ > *trans*-$CH_3$–CH=CH–$CH_3$ > $(CH_3)_2C=CH_2$ > $CH_3$–$CH_2$–CH=$CH_2$, which is apparently determined by the nucleophilic character of the double bond in the alkene molecule and by steric factors. The presence of electron-acceptor substituents on the allyl carbon atom decreases the reaction rate considerably. A similar conclusion was reached[56] in a study of the kinetics of the reactions of alkenes with different structures with N,N-dimethyl-*p*-nitrosoaniline, which established that the highest rate in this reaction is shown by alkenes with the isostructure, containing an internal double bond on the tertiary carbon atom. A study of the kinetics of the reaction showed that it is formally of first order with respect to both reagents in a large excess of one of them.

To prove that a reaction is an ene reaction, it is important to establish the exact position of the hydroxylamine group in the chain or, if this is impossible because of the ease of oxidation of the hydroxylamine, to establish the position of the resulting nitroxide radical from the hyperfine structure of the EPR spectrum. Thus the presence or absence of hydrogen on the α-carbon atom (relative to the nitroxide group) has a significant influence on the EPR spectrum. Contradictory data are also obtained with this approach, however. Thus the product of the reaction of allyl halides with trifluoronitrosomethane according to some authors[55] is the one adduct (XXI) and according to others[20] the isomeric product (XXII).



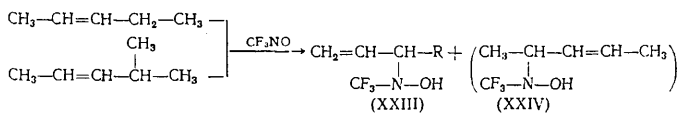
(XXI) (XXII), X=Cl, Br

Nevertheless, many authors give irrefutable data which indicate that the ene adduct is formed, that is that the nitrogen of the nitroso-group is added to the carbon of the double bond with the simultaneous transfer of the allyl hydrogen to the oxygen of the nitroso-group and prototropic displacement of the double bond. One interesting proof is the formation of a cyclic hydroxylamine by an intramolecular ene reaction in nitrosoalkenes:[57]



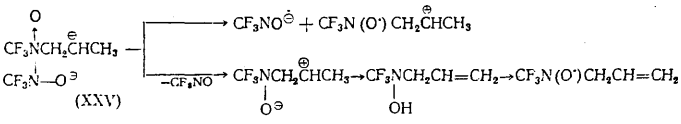
The nitroso-group adds on to the α- or β-unsaturated carbon atom, depending on the nature of the allyl hydrogen atom. The primary and secondary γ-protons are approximately equally readily transferred to the oxygen atom of the nitroso-group,[55] and the proton of the methine group is much more difficult to remove. Thus pent-2-ene reacts with trifluoronitrosomethane to give a mixture of isomers (XXIII) and (XXIV) as a result of the transfer of a hydrogen atom from the $CH_3$ and $CH_2$ groups respectively, whereas with 4-methylpent-2-ene, where there is a choice between CH and $CH_3$ groups, only compound

(XXIII), with R = iso-$C_3H_7$, is formed.



For alkenes with the iso-structure, the position at which the nitroso-group is added depends not only on the nature of the allyl hydrogen but also on the electronegativity of the carbon of the double bond. Thus an analysis of the EPR and NMR spectra[58] established that nitrosobenzene reacts with 2-methylpent-2-ene to give an ene adduct at the =CH— fragment of the alkene molecule.

Different views of the mechanism of formation of the ene adducts of nitroso-compounds with alkenes, in particular of the structure of the intermediates, have been put forward. In Ref.20 it is stated that the reaction of a nitroso-compound with an alkene gives initially a 2:1 donor–acceptor complex,[25] in which the alkene is generally the donor, and the nitroso-compound the acceptor. An exception is provided by acrylates or vinyl compounds with strong electron-acceptor substituents, where at increased temperatures the unsaturated compound may act as the electron acceptor, and the nitroso-compound as the electron donor. The decomposition of this complex to give 1:1 adducts, for example for the reaction of trifluoronitrosomethane with propene, takes place according to the scheme:



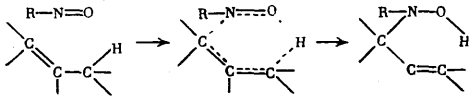
The author cited bases his idea of a single redox mechanism for this process on the reactivity of alkenes with different structures, which is consistent with the values of the ionisation potentials, characterising the donor properties of the alkene,[59] and also with the tendency of the alkenes to form charge-transfer complexes with other acceptors,[60] and the reactivity of alkenes in reactions with electrophilic reagents.[61]

According to another opinion,[50] the reaction involves the formation of a four-membered oxazetidine ring, which subsequently breaks down to give the hydroxylamine derivative.

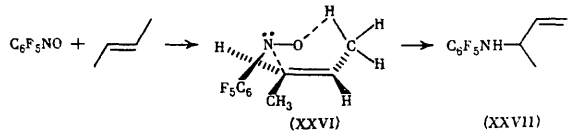
These ideas have been criticised,[55] however, and as proof of the absence of the zwitterion intermediate (the bipolar ion (XXV) in Ref.20), the reaction with β-pinene, which is not accompanied by rearrangement, is considered.

The heterolytic, and not homolytic, character of the first stage of the reaction of a nitroso-compound with an alkene is confirmed by the addition to the alkene carbon, and not to the carbon which was initially the allyl carbon.

In Ref.25 it is considered that the intermediate state of the ene reaction is a six-membered internal associate, and this reaction is regarded as a familiar "synchronous transfer" reaction.

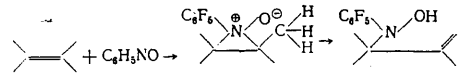


According to these ideas, the formation of the secondary amine (XXVII) as the product of the reaction of pentafluoronitrosobenzene and *trans*-but-2-ene is explained by the role of the steric factors in the intermediate state (XXVI) of the ene reaction.[25]



The recent increased interest in ene reactions with different enophiles such as oxygen,[62–64] triazolinediones,[65,66] and compounds with S=N bonds,[67] however, has led to a re-examination of the idea of a six-membered intermediate state.

Thus a study of the isotope effects produced by the deuteriation of tetramethylethylene led to the conclusion that its reaction with pentafluoronitrosobenzene takes place in two stages,[52] and that the first stage of the process, which is the limiting stage, gives a three-membered cyclic compound, an aziridine oxide, which subsequently undergoes rapid splitting of the C–H and C–N bonds to give the ene product:



The transformations of the ene product, including the formation of nitroxide radicals, will be examined below. It has been suggested, however, that nitroxide radicals in the reactions of nitroso-compounds with alkenes are not necessarily formed by the oxidation of an intermediate alkenylhydroxylamine, particularly since paramagnetic species have also been obtained in the reactions of nitroso-compounds with unsaturated compounds not containing allyl hydrogen, that is in cases where the formation of an ene adduct is impossible. These species have been observed in reactions with styrene,[22] trifluorostyrene,[21] vinyl acetate, and derivatives of acrylic acid (these paramagnetic species were assigned the corresponding radical–cation and radical–anion structures[20]).

Thus a study[68] of radical processes in a nitroso-compound–alkene system (for the reactions of nitrosobenzene and *p*-chloronitrosobenzene with oct-1-ene, cyclohexene, butadiene, and cycloheptatriene) leaves open the question of the mechanism of the first stage of the process. The following reaction scheme is given:

$$ArNO + CH_2{=}CHR \rightarrow ArN(O^{\cdot})CH_2{-}\dot{C}HR \quad (1)$$

$$2ArN(O^{\cdot})CH_2{-}\dot{C}HR \rightarrow [ArN(O^{\cdot})CH_2{-}CH(R){-}]_2 \quad (2)$$

$$ArNO + ArN(O^{\cdot})CH_2{-}CH{-}\dot{C}HR_2' \rightarrow ArN(O^{\cdot})CH_2CH{=}CR_2' + ArNHO^{\cdot} \quad (3)$$

$$ArNO + ArN(O^{\cdot})CH_2{-}\dot{C}HR \rightarrow ArN(O^{\cdot})CH{=}CHR + ArNHO^{\cdot} \quad (4)$$

$$ArNO + ArN(O^{\cdot})CH_2{-}\dot{C}HR \rightarrow ArN(O^{\cdot})CH_2CH(R){-}N(O^{\cdot})Ar \quad (5)$$

The biradical formed according to Eqn.(1) reacts rapidly according to Eqns.(2)–(5) to give other radicals which are then transformed more slowly by disproportionation, recombination, or reaction with the starting materials to give nitrones, hydroxylamines, azoxybenzenes, etc.

The approach in Ref.68 to the determination of the mechanism of the primary stage of the reactions of nitroso-compounds with alkenes appears too cautious; the nitroxide radicals are most probably formed by the oxidation of the intermediate alkenylhydroxylamine by the nitroso-compound. Data confirming this view are given below.

### 3. The Mechanism of the Subsequent Stages of the Reactions of C-Nitroso-compounds with Alkenes

The examination of the mechanism of the subsequent stages of the reactions of nitroso-compounds with alkenes should essentially be concerned with the reactions of disubstituted

hydroxylamines with nitroxide radicals, that is the intermediates whose formation (at least one of them) is postulated by most authors.

*a) Reactions of disubstituted hydroxylamines*

The chemistry of alkylarylhydroxylamines and alkenylarylhydroxylamines has been little studied; most data relate to their decomposition and oxidation.

The chief products of the thermal decomposition of these compounds are a nitrone and a secondary amine,[69,70] formed by the disproportionation of two moles of the disubstituted hydroxylamine. It has been confirmed[13] that the decomposition is of second order with respect to the hydroxylamine, and that the decomposition rate depends on the nature of the substituent; electron-donor substituents increase the reaction rate. A study of the thermal decomposition of *p*-substituted N-phenylhydroxylamines showed that the reaction products are nitrones and azoxy-arenes.[13] Another possible direction of transformation of substituted hydroxylamines when heated is dehydration to give an azomethine.[48]

However, the most important reaction of alkenylarylhydroxylamines as intermediate products of the reaction of nitroso-compounds with alkenes is undoubtedly their oxidation by oxygen in the reaction mixture or, if it is not present, by the unreacted nitroso-compound.

The mechanism of this reaction can be considered. Thermodynamic studies have shown[71,72] that stable radicals X$^{\cdot}$ may be produced by the removal of only mobile hydrogen by the reaction:

$$RN{=}O + XH \rightarrow RNHO^{\cdot} + X^{\cdot} \qquad (6)$$

The low dissociation energy of the OH bond in alkenylaryl- and alkenylalkylhydroxylamines[73] facilitates this reaction. Reaction (6), which involves molecular homolysis by the rupture of a simple bond under the influence of the reagent, in the opinion of the authors of Ref.72 corresponds more closely to the experimental data than two other reactions which may give radicals, namely the reaction of two π-systems to give biradicals, and donor–acceptor electron exchange to give two radicals or a radical–ion.[74] Under certain conditions, the last type of homolysis is probably involved in the reactions of nitroso-compounds with unsaturated compounds not containing γ-protons.

Direct proof of the formation of nitroxide radicals in the reactions of nitroso-compounds with hydroxylamines has been given.[75]

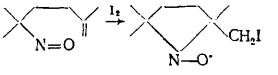
Evidence of a reaction of type (6) between a nitroso-compound and an N-substituted hydroxylamine is also provided by recent data on the formation of nitroxide radicals in the reactions of nitroso-compounds with other compounds containing active hydrogen: carbonyl compounds capable of enolisation, thiols, and phenols,[54] thiophenols,[76], imines in the enamine tautomeric form,[77] diketones,[78] etc.

At the same time, the importance of the photolysis of nitroso-compounds in the production of nitroxide radicals in a reacting system has been emphasised:[72] the light source may be natural light or ordinary artificial laboratory illumination.

$$RN{=}O \xrightarrow{h\nu} R^{\cdot} + NO^{\cdot}$$
$$R^{\cdot} + RNO \rightarrow R_2NO^{\cdot}$$

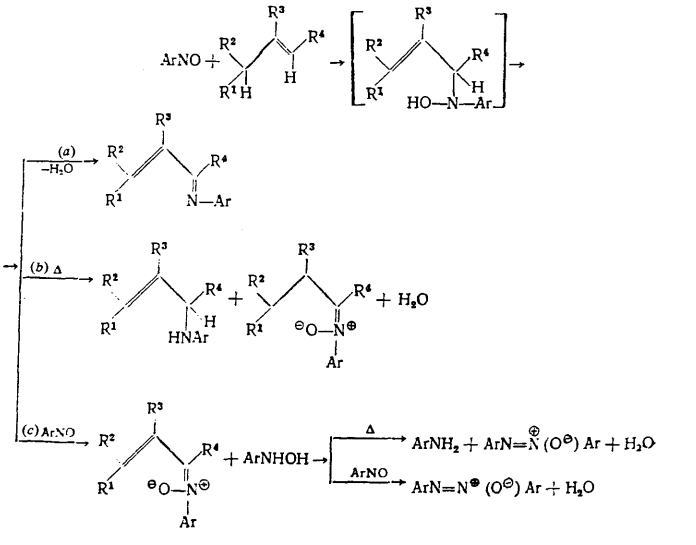
Nevertheless, most authors attribute the formation of nitroxide radicals in the reactions of C-nitroso-compounds with alkenes to the oxidation of an intermediate hydroxylamine,[20,25,28,55,57,58] the oxidant usually being the nitroso-compound itself (when the reaction is carried out in an inert medium), although if the aim is to obtain the nitroxide it is possible to introduce oxidising agents specially, for example silver oxide[79] or iodine.[80]

The last paper is of particular interest, since it proposes a general method for synthesising cyclic nitroxides by the action of iodine on δ, ε-unsaturated nitroso-compounds.



There are very few published data on the final oxidation products of disubstituted hydroxylamines. The final products of the oxidation of N-benzyl-N-phenylhydroxylamine by different *p*-substituted nitrosobenzenes are the α,N-diphenylnitrone and *p*-substituted azoxybenzenes.[13] When the aromatic nitroso-compound contains strong electron-donor substituents, an appreciable quantity of derivatives of primary amines is found in the reaction mixture, in addition to azoxybenzenes.

From their experimental data and an analysis of published data, the following scheme was proposed for the reactions of nitroso-compounds with alkenes containing an allyl hydrogen atom:[13]



According to this scheme, the first stage of the reaction is an ene reaction, leading to the formation of an alkenylarylhydroxylamine, which subsequently undergoes transformations characteristic of disubstituted hydroxylamines: oxidation (*c*), thermal decomposition (*b*), and dehydration (*a*) to give the nitrone, azoxybenzene, amines, and an azomethine.

An undoubted advantage of the proposed scheme is that the authors tried to use known reactions to explain the transformation of N-substituted hydroxylamines into products which in the opinion of many workers are the final products of the reactions of nitroso-compounds with alkenes containing an allylic hydrogen atom.

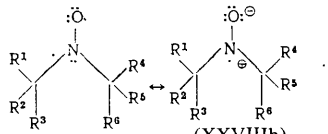
At the same time, the scheme has a serious shortcoming, in that it ignores the fact that nitroxide radicals are formed in the reactions of nitroso-compounds with alkenes, and the relationship between the structures of the radicals and the final products.

Since there are no published data on this relationship, those reactions of nitroxide radicals which can apparently take place during the formation of the products of the reactions of nitroso-compounds with alkenes will be considered.

*b) Reactions of nitroxide radicals*

The chemistry of nitroxide radicals is a widely studied field, to which a large contribution has been made by Soviet scientists.[81–83] The thermodynamic stability of nitroxide radicals

is determined by the degree of delocalisation of the unpaired electron between oxygen and nitrogen (XXVIIIa, b); for dialkyl nitroxides the delocalisation energy is ~30 kcal mole$^{-1}$.



(XXVIIIa) (XXVIIIb)

In general, the stability of the free radicals correlates well with the dissociation energy of the bonds broken on radical formation.

Thus reactions such as the oxidation of hydroxylamines having a low energy of removal of the hydrogen of the hydroxyl group[73] or the "spin capture" of carbon-centred radicals by spin traps such as nitroso-compounds and nitrones[84] lead to the rapid formation of nitroxide radicals.

An important condition for the stability of disubstituted nitroxide radicals is the absence of hydrogen atoms on the α-carbon atom.[85] At the same time, monosubstituted nitroxides and dialkyl or alkyl aryl nitroxides containing methyl, methylene, or methine groups in the α-position, that is the radicals most frequently formed in the reactions of nitroso-compounds with alkenes, are generally insufficiently stable, and undergo recombination and disproportionation, and also react with reagents or intermediates in the reaction system.

The chemical properties, in particular the ability to undergo recombination and disproportionation, of mono- and disubstituted nitroxides can be considered separately.

*Monoaryl and monoalkyl nitroxides.* The oxidation of N-phenyl-hydroxylamine by nitrosobenzene to give the phenyl nitroxide radical was first reported in Ref.86; the study of this reaction in different media shows that it gives azoxybenzene; the intermediate is a radical–anion in the presence of a strong base, and a nitroxide radical in the absence of a strong base.

A study of the kinetics of the decomposition of methyl, isopropyl, t-butyl, and phenyl nitroxides in solution[71] established that both reversible disporportionation to hydroxylamino- and nitroso-derivatives, and slower recombination to give an azoxy-compound, take place. For the phenyl derivative, the equilibrium constants and rates of the following reactions were calculated:

$$2C_6H_5NHO^{\cdot} \overset{K}{\rightleftharpoons} C_6H_5NHOH + C_6H_5NO \qquad (7)$$

$$2C_6H_5NHO^{\cdot} \xrightarrow{k_{azo}} C_6H_5N{=}NC_6H_5 + H_2O \qquad (8)$$

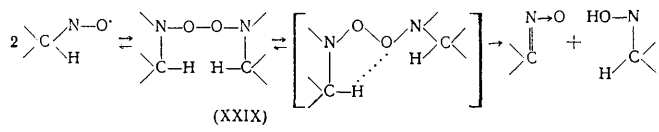
$$\downarrow O$$

The authors assume, however, that direct condensation of nitrosobenzene and N-phenylhydroxylamine to give azoxybenzene may take place.

At the same time, a study of the catalysis of this reaction using $Fe^{2+}$ and $Fe^{3+}$ salts[87] showed that the formation of azoxybenzene undoubtedly involves the dimerisation (recombination) of the nitroxide radical, that is according to Eqn.(8).

Important results were obtained in a study of the dependence of the stability of nitroxide radicals on the concentration in the solution. The rate of the decomposition of these radicals increases with decrease in their concentration.[71,86]

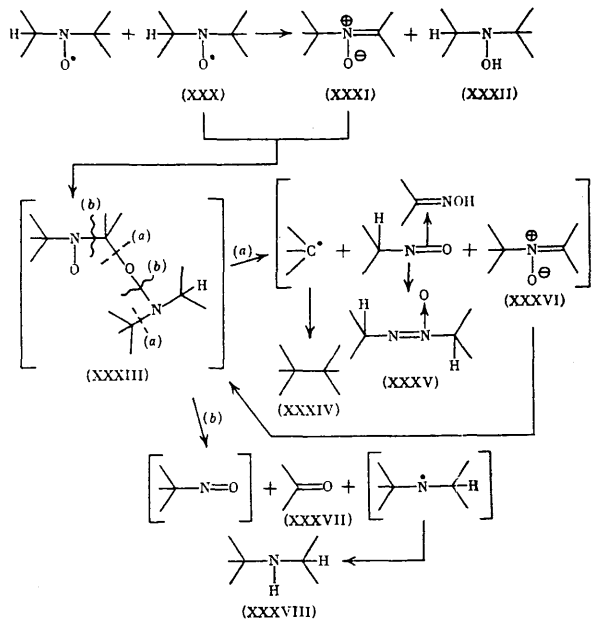
*Disubstituted nitroxide radicals.* The most stable radicals are di-t-alkyl nitroxides. In contrast to this, nitroxides having at least one hydrogen atom on the α-carbon atom usually disproportionate to hydroxylamines and nitrones. According to Refs.88 and 89, the mechanism of this reaction involves the dimerisation of the nitroxide and the subsequent slow decomposition of the diamagnetic dimer:



(XXIX)

The participation of the α-hydrogen atom in the limiting stage of the process was proved by replacing it with deuterium. The reaction shows a strong isotopic effect ($k_H/k_D \cong 9$).[93] At the same time, the structure of the dimer (XXIX) is not considered to have been proved,[90,91] since a thermochemical examination of the process[88,91] indicates that the formation of the O–O bond is endothermic, with an energy expenditure of 28 kcal mole$^{-1}$. The formation of at least three types of dimer with O–N, O–C, and N–N bonds has been reported.[92]

In a study of the decomposition of t-butyl isopropyl nitroxide radicals, doubt was cast[93] on the mechanism involving dimerisation, and the following scheme was given for the process:

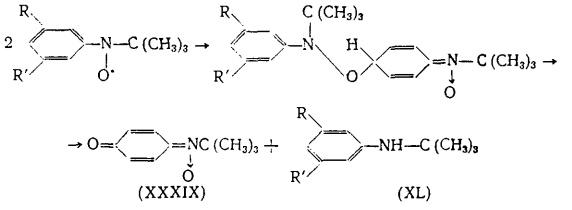


(XXX) (XXXI) (XXXII) (XXXIII) (XXXIV) (XXXV) (XXXVI) (XXXVII) (XXXVIII)

According to this scheme, the disproportionation of the nitroxide radicals (XXX) gives a hydroxylamine (XXXII) and a nitrone (XXXI), which being an excellent spin trap reacts with the original nitroxide radical to give an unstable secondary radical (XXXIII); decomposition of the latter gives products such as the alkane (XXXIV), the dimer of the nitroso-compound (XXXV), the oxime (XXXVI), the ketone (XXXVII), and the secondary amine (XXXVIII). Under certain conditions, the nitrone may be formed not by the disproportionation of the nitroxide but by its oxidation by an oxidant present in the system; this takes place in the formation of dibenzyl nitroxide from dibenzylhydroxylamine.[94]

Aryl t-alkyl nitroxides are much less stable than di-t-alkyl nitroxides. At first sight this fact is difficult to explain, since in the aryl derivatives the phenyl ring provides an additional region for delocalisation of the unpaired electron, and this should have led to an increase in the stability of the radical. The reason for this phenomenon is the dimerisation of the aryl t-alkyl nitroxides by the formation of a bond between the oxygen atom of the nitroxide and the *para*- or

*ortho*-positions of the benzene ring with subsequent decomposition of the dimer to the *p*-benzoquinone-N-t-alkylimine (XXXIX) and N-t-alkylaniline (XL).[95-100]



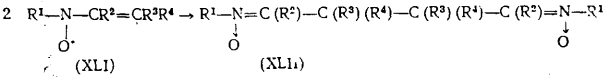
(XXXIX) (XL)

The formation of the dimer is inhibited by the presence of substituents in the *ortho*-position, which prevents the delocalisation of the electron density of the nitroxide group and hence decreases the spin density in the aromatic ring.[98] Bulky substituents in the *para*- or *meta*-positions also stabilise the radical as a result of the production of steric hindrance for radical attack.[95,98,100]

The influence of the structure of substituents on the stability of nitroxide radicals is effectively illustrated not only by their decomposition but also by their ability to recombine with hydrocarbon radicals. Thus aromatic nitroxides react with triphenylmethyl,[101] whereas nitroxides with aliphatic substituents do not react with it.[102]

Vinyl nitroxide radicals represent another important type of paramagnetic species for the chemistry of homolytic processes taking place in the reactions of nitroso-compounds with alkenes. These radicals may be formed either according to the scheme proposed in Ref.68 or by the oxidation of nitrones containing a hydrogen atom in the β-position, which in the opinion of many authors are among the main products of the reactions of nitroso-compounds with alkenes. As might have been expected, vinyl nitroxides are further stabilised by the delocalisation of the unpaired electron by conjugation with the vinyl group. At the same time they are fairly reactive.[103]

The recombination of vinyl nitoxide radicals (XLI) to give nitrones (XLII) takes place by the formation of a C–C bond in the β-position.



(XLI) (XLII)

Nitroso-compounds, nitrones, dienes, etc. also add on to the β-position of the vinyl group. The length of the chain is increased, with the formation of substituted nitroxide radicals.[103] These data illustrated a familiar fact in the chemistry of nitroxide radicals: the dependence of their stability and reactivity on their structure is determined by a combination of thermodynamic and kinetic factors, that is the degree of delocalisation of the unpaired electron and the steric hindrance at the atoms with a high spin density.

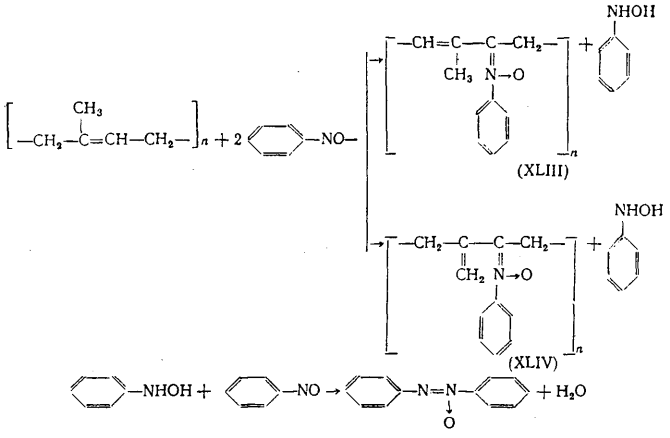
Thus analysis of published data on the reactions of nitroxide radicals shows that the compounds detected in the products of their recombination, disproportionation, oxidation, etc. include many of those compounds (azoxybenzenes, hydroxylamines, nitrones, secondary amines) which are regarded as the main products of the reactions of nitroso-compounds with alkenes. This confirms that these products may be formed in the reactions of C-nitroso-compounds with alkenes via nitroxide radicals as intermediates.

At the same time, the indefinite nature of conclusions about the structure of the reaction products is apparently due to the wide range of possible directions for the reactions of nitroxide radicals, characteristic of all homolytic processes, the results of which depend on the structure of the starting materials and on the reaction conditions. These reactions generally have a low selectivity and often give mixtures of products.

## IV. CHARACTERISTIC FEATURES OF THE REACTION OF NITROSO-COMPOUNDS WITH DIENE POLYMERS

The study of the reaction of nitroso-compounds with diene polymers to determine the reaction mechanism is difficult, because of the difficulty of isolating and identifying the functional fragments; on the other hand, however, this study extends the possibility of estimating the changes in the dimensions of the molecules taking place in the course of the reaction.

The reaction of nitroso-compounds with natural *cis*-1,4-polyisoprene was first studied in Ref.26, and in more detail in Ref.104, where a reaction scheme was proposed, based on the reaction of three moles of the nitroso-compound with one monomer unit, leading to the formation of two isomeric conjugated nitrones and azoxybenzene.



(XLIII)

(XLIV)

The authors cited, however, could not decide between the adduct structures (XLIII) and (XLIV).

In a development of these ideas, it was concluded[105] that the nitrone of "iso-rubber"† (the terminology of the authors cited) can be obtained in pure form only by carrying out the reaction without heating, in a nitrogen atmosphere.

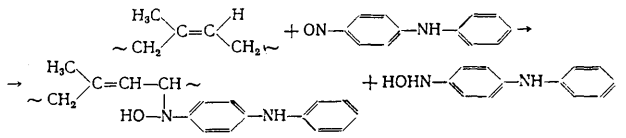
This scheme was adopted by various workers as a possible mechanism of structure formation in saturated rubbers with C-nitroso derivatives[106] and of the modification of polyisoprene by N-substituted *p*-nitrosoanilines.[107]

Alternative structures suggested for the functional fragment formed in the reaction of polyisoprene with N-methyl-N,4-dinitrosoaniline are the anil structure,[48] and in the reaction with *p*-nitrosodiphenylamine the secondary amine[6,108] and hydroxylamine[109] structures; in the last case the reaction product is not the ene adduct but the product of the addition of the nitroso-group to the allyl carbon (XLV).

The authors of Ref.48 describe the mechanism of the process as ene synthesis with subsequent dehydration of the intermediate alkenylarylhydroxylamine and the formation of a Schiff base, whereas in Ref.109 the mechanism of the process is described as molecular homolysis with the removal of allyl hydrogen and the subsequent recombination of the radicals

†The term iso-rubber refers to *cis*-1,4-polyisoprene with isomeric location of the double bonds in the 1,5- and 1,4-positions.

to give diphenylaminohydroxylamine in the free state or combined with the polymer chain.

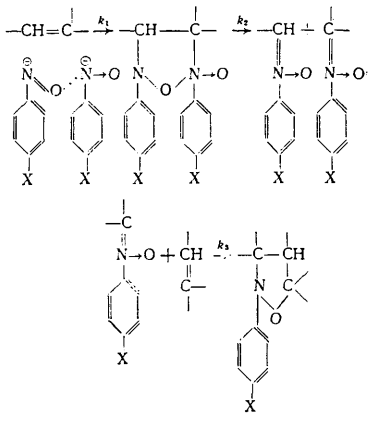


The main characteristic of the reaction of a nitroso-compound with a polydiene is the degradation of the polymer chain. In the case of the reaction with low-molecular-weight alkenes, only the authors of Refs.18 and 26, who describe the reaction of styrene with nitrosobenzene, note the possibility of rupture of the hydrocarbon chain, whereas for the diene polymer the effect of degradation is marked.

However, although in Ref.109 it is suggested that the nitroso-compound initiates the thermo-oxidative degradation of the polymer at a high temperature (143 °C), it has been shown[100–112] that rupture of the polymer chain takes place as a result of the chemical reaction of the polydiene with the nitroso-compound, and that there is a good correlation between the nitroso-compound : polyene molar ratio and the molecular mass of the degradation product.[110–113] Conditions have been found for the synthesis of oligoisoprenes over a wide range of molecular masses.[114,115]

Comparison of the number-average molecular masses of the original and reacted polyisoprene with the number of functional groups combined with the rubber shows that an average of about two molecules of the nitroso-compound is added on for every rupture of the macromolecule.[113] A more detailed analysis of the molecular structure of the oligoisoprenes formed[116] showed that the maximum of the distribution of the oligomer with respect to functionality corresponds to 2, and the molar concentration of bifunctional molecules reaches 40. At the same time, an appreciable quantity of mono-, tri-, tetra-, and pentafunctional molecules, and a small quantity of molecules of higher functionality, were detected in the oligomer.

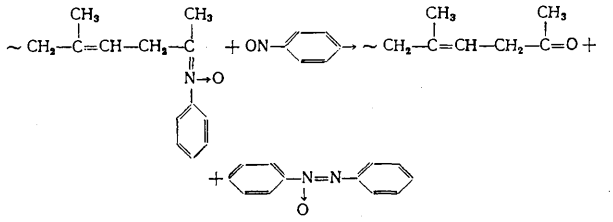
These experimental data, together with the results of a study of the kinetics of the reaction (first order with respect to the nitroso-compound in an excess of the polymer)[113] and an analysis of the structure of the final products[117] led to the proposal of the following scheme for the degradation and subsequent branching of the polymer molecules:



X = N($C_2H_5$)$_2$, $NHC_6H_5$

According to this scheme, the final reaction products are nitrones or the products of their transformation.[113,117]

At the same time, Japanese workers isolated,[110] in addition to degradation products which were also identified as polymeric nitrones, side products: an aldehyde (or ketone) and azoxybenzene.



In contrast to the reaction in solution, the reaction of *cis*-1,4-polyisoprene with *p*-nitrosodiphenylamine in the mass at high temperatures is often accompanied by the formation of a cross-linked rubber. According to Ref.109, structure formation takes place by the recombination of the hydrocarbon polymeric radicals produced in this reaction. A specific feature of the chemical modification of diene polymers by so-called small additives is that the process is carried out in a large excess of one of the reagents (the polymer), so that some of the reactions which are observed in the reaction of equimolar quantities of the nitroso-compound and the alkene or in an excess of the nitroso-compound cannot be observed in this case.

Even with allowance for this characteristic feature, however, and also for the specific features of the transformations in the polymer chains, it must be said that the schemes given for the reactions of nitroso-compounds with diene polymers are oversimplified, and do not take critical account of the extensive experimental material accumulated in the study of the mechanism of the reaction of a nitroso-compound with low-molecular-weight alkenes, so that they require, at the least, serious refinement.

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Progress in fundamental and applied studies of the use of C-nitroso-compounds as paramagnetic inhibitors, spin traps, stabilisers and modifiers of rubber and plastics, and promoters of the reaction of rubber with technical carbon has stimulated interest in the investigation of the mechanism of the reactions of nitroso-compounds with alkenes. For this reaction, as for other processes involving the formation of extremely reactive intermediates, the possible directions of the reaction and the structures of the final products depend on the nature of the substituents in the reagents and on the reaction conditions. In this respect, each new study carried out on individual representatives of both classes of compound extends the picture of the reaction as a whole.

Many general features of the reactions with alkenes with and without an allyl hydrogen atom have now been established, however. These general characteristics apparently include the heterolytic character of the first stage of the addition, attack by the nitroso-compound on the carbon atom of the double bond, the formation of paramagnetic species in one of the subsequent stages, etc.

The achievements in the application of C-nitroso-compounds have increased interest in their reactivity and the mechanism of their reactions with alkenes; the data obtained have in turn led to new ideas for the practical utilisation of this reaction.

Thus the experimentally observed rupture of the hydrocarbon chain in the reaction of a polymeric alkene with a nitroso-compound has made it possible to synthesise for the

first time an oligoisoprene with the *cis*-structure with functional polar groups, that is a material which has not yet been prepared by polymerisation methods. The paramagnetic species in the reaction system under certain conditions can be used to initiate the radical grafting of unsaturated polar compounds to an unsaturated hydrocarbon substrate.

There is no doubt that this extremely important reaction in organic chemistry will continue to attract the attention of research workers for a long time.

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# Structural Vacancies in Compounds of Variable Composition

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The results of studies of compounds of variable composition based on the high-melting metals of the IVa and Va subgroups (oxides, nitrides, carbides, oxide carbides, oxide nitrides, carbide nitrides) have been systematically examined. Problems of atomic ordering in these compounds are discussed, including the development of an inhomogeneous structure and the control of the vacancy concentration while retaining the original chemical composition and type of crystal structure at high pressures and temperatures. The thermodynamics of the formation of structural vacancies in compounds of variable composition are discussed.
The bibliography includes 123 references.

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## I. INTRODUCTION

Several new compounds of both fixed and variable composition, including compounds with an ordered structure, have been discovered in the last 15–20 years in many well known binary systems of the M–C, M–N, and M–O type (where M is a transition metal from subgroup IVa or Va). Many were obtained by controlling the concentration of vacancies in the crystal lattice, and their distribution. This is true, in particular, of the compounds of the interstitial phase type based on high-melting metals.

The most characteristic feature of compounds of variable composition of this type is the presence of a close-packed sublattice of the pure metal, which acts as a matrix for different atoms accommodated in its interstitial cavities and forming a non-metal sublattice. In this sense the pure metal can be formally treated as a special state of the compound of variable composition in which all the interstitial sites are vacant. In this case the vacant interstitials should be treated as a species equivalent to an interstitial atom rather than as a simple hole in the crystal lattice. When the non-metal sublattice is partially filled the vacant interstitial sites (or structural vacancies) can diffuse through the lattice and behave in some respects like real interstitial atoms.

Structural vacancies, like interstitial atoms, can affect practically all the properties of compounds of variable composition of the interstitial phase type.[1-8] Therefore the defects in the crystal structure should be treated as one of the most important properties of the carbides, nitrides, and oxides of the transition metals, and also of the solid solutions based on them.[1,4-15] These substances, which have a wide homogeneity region, can be described as chemical formations whose composition includes, in addition to metal atoms and non-metal atoms, structural vacancies[5,8] in the non-metal or in the metal sublattice, or in both sublattices simultaneously. It was pointed out[4] in 1969 that vacancies (like metal atoms and non-metal atoms) are independent components of the system and they can affect its properties even more markedly than the atoms.

In addition to "compounds of variable composition", the term "non-stoichiometric compounds" is now generally used in scientific publications, but not always with the same meaning. It has been suggested[4] that the new term is incorrect, since a non-stoichiometric compound has a fixed composition though it is represented by a formula with fractional indices. If we adopt this point of view we must classify the compound $Cu_{31}Sn_8$ (of constant composition) as stoichiometric or as non-stoichiometric according to the method of writing the formula (since simplification produces fractional indices: for example ($Cu_{15.5}Sn_4$ or $Cu_{3.875}Sn$). The same applies to the many organic compounds with a molecular structure, often with a complex chemical composition, which can be expressed by formulae with integral or with fractional indices. Nevertheless their compositions obey the law of multiple proportions, and the compounds are not non-stoichiometric.

In a realistic and soundly based definition[5] of a "non-stoichiometric compound" the concept is associated with the perturbation of the ideal crystal structure. Any compound having a geometrically regular crystal lattice is classified[5] as stoichiometric.

We consider that any compound of fixed composition and having a lattice shown (by diffraction methods) to be ideal should be classified as stoichiometric. The integral indices in the chemical formula of a stoichiometric compound can have any value (not necessarily small), determined from chemical analysis and structural studies. The term non-stoichiometric should be applied to compounds having a homogeneity region, whose width can be determined by analytical methods (mainly, compounds with structural vacancies in their unit cell). The distribution of atoms of different kinds (or of atoms and structural vacancies) in each of the sublattices of a non-stoichiometric compound can be random or ordered.

Clearly, the terms "compound of variable composition" and "non-stoichiometric compound" used in scientific publications have equivalent meanings. The carbides, nitrides, and oxides of the transition metals have wide homogeneity regions and are most correctly referred to as non-stoichiometric compounds of variable composition of the interstitial phase type. This description most fully reflects the special features of the crystalline structure of these substances (the position of the added atoms in the interstitial sites of the metal sublattice, and the presence of a homogeneity region), but the term is too long, and in this review we shall use the shorter term "compounds of variable composition".

## II. ATOMIC ORDERING IN COMPOUNDS OF VARIABLE COMPOSITION

It was initially assumed that structural vacancies in the crystal lattice of compounds of variable composition in their homogeneity region are randomly distributed. This belief applied, in particular, to the monocarbides and the mononitrides of the transition metals of subgroups IVa and Va over the whole of their temperature region of existence, as shown in the standard monographs.[1,9,11,12,16] However, ample evidence was subsequently found of the existence of both short-range and long-range order in the crystal lattice of these compounds and of their solid solutions.

Using mainly crystallographic arguments Parthe and Yoon[17] defined eight possible types of ordered structures in carbides: $M_2C$, $M_3C_3$, $M_8C_5$, $M_3C_2$, $M_4C_3$, $M_5C_4$, $M_6C_5$, and $M_8C_7$ (where M = Ti, Zr, Hf, V, Nb, Ta). Most of these have already been prepared. In multi-component compounds and in solid solutions the number of possible variants of the structure is, of course, even greater. In the systems M–C, M–N, M–C–O, M–N–O, and M–C–N more than 70 ordered phases have already been discovered: they are formed from the basic structures with face-centred cubic (FCC), body-centred cubic (BCC), and close-packed hexagonal (CPH) crystal lattices. The many superstructures listed in Table 1 were identified by using high-sensitivity diffraction methods (especially neutron diffraction) and lengthy heat treatments (hundreds of hours) at relatively low temperatures (1300 K or less).

The kinetics of the order–disorder transition are largely determined by the previous history of the sample. Thus, the ordering of non-stoichiometric compounds was found[69] to be assisted by the addition of hydrogen. A similar effect was observed[70] after the simultaneous introduction of small amounts of oxygen and nitrogen into the crystal lattice of the hexagonal carbides $Nb_2C$ and $V_2C$. Reports that ordering is assisted by additions of oxygen, nitrogen, and hydrogen appear also in Refs.71 and 72. In the non-stoichiometric compounds of the V–C system the order–disorder transition was found[73] to depend also on the micro-structure of the sample. Furthermore, two different cubic forms of titanium monoxide $TiO_{1.00}$ have been reported[27] (one of the NaCl type, with a random distribution of vacancies, and another with a partially ordered distribution of vacancies and a 3 times greater lattice constant), stable at 1500–2100 K and 1250–1500 K respectively. A third, monoclinic modification of $TiO_{1.00}$ with a fully ordered distribution of vacancies is stable at temperatures below 1250 K. However, other workers prepared compounds of the $TiO_y$ type at 1270 K [74] and 1070 K,[75] but failed to observe the ordering reported[26,27] for the compound $TiO_{1.00}$ (and also for other $TiO_y$ compositions). Only one cubic structure (NaCl type) was found in the entire homogeneity region by using "preparations in X-ray diffraction equilibrium".

The data in Table 1 suggest that ordering in the non-stoichiometric monocarbides of the group V transition metals produces mainly phases of composition $M_6C_5$ having monoclinic and trigonal structures. A structural feature common to all ordered phases of the non-stoichiometric monocarbides of the group IV and V transition metals is an alternation of completely filled and partially filled carbon planes in the $[111]_{NaCl}$ or equivalent directions.

In the ordered lower carbides $M_2C$ the characteristic feature is an alternation (in the direction perpendicular to the *c* axis) of carbon planes filled to different extents with carbon atoms.

We also note from Table 1 that the ordered phases of non-stoichiometric cubic titanium, vanadium, and niobium mononitrides have tetragonal structures and differ substantially from the corresponding ordered carbides. In the unit cell of the ordered titanium and niobium nitrides the vacancies are accommodated in the sites of a body-centred tetragonal lattice. In the cubic monoxides different ordered phases can be formed according to the oxygen content and the heat treatment conditions: they have cubic, tetragonal, rhombic, or monoclinic lattices.

The overall conclusion from the data in Table 1 is that ordering phenomena are relatively common in non-stoichiometric compounds of the interstitial phase type, and they are associated with a redistribution of the non-metal atoms over the octahedral interstitials of the metal sublattice.

## III. INHOMOGENEOUS STRUCTURE IN COMPOUNDS OF VARIABLE COMPOSITION

The previous history of the sample, which affects the rate of the order–disorder transition, includes the impurities initially present in the materials or introduced during the synthesis, the type and duration of the heat treatment adopted (homogenising, recrystallising, stress relieving), and the chosen cooling regime.

These effects are clearly illustrated by a full and detailed study of short-range and long-range order in the non-stoichiometric niobium carbide $NbC_y$ by NMR,[57,76,78] structural neutron diffraction, X-ray diffraction,[57,58] and magnetic susceptibility.[57,77] It was found that even $NbC_y$ samples quenched from 1800–2300 K contain some short-range order, but the degree of ordering is small. This increases as the temperature is lowered to the transition point, but no long-range order is observed. The structural phase transition, associated with ordering of the carbon atoms and of the structural vacancies in the non-metal sublattice of $NbC_y$, begins near 1300 K. The NMR spectra for the $^{93}Nb$ nuclei in $NbC_y$ and the magnetic susceptibility of the niobium carbide samples containing the ordered $Nb_6C_5$ phase are markedly different from those for the disordered state of niobium carbide.[76–78]

On the other hand the NMR spectra and the magnetic susceptibility are almost unaffected by the amount of ordered phase in the sample, i.e. they are insensitive to the long-range order parameter. It follows[57,77] that in niobium carbide samples containing an ordered phase and prepared with different heat treatment regimes the short-range order parameter $\alpha$ for $NbC_y$ of any composition is almost the same and close to the maximum possible value. This conclusion is confirmed by calculations of $\alpha$ from magnetic susceptibility data.[57,77] Hence the equilibrium state of niobium carbide in the two-phase region near the transition temperature has a high proportion of short-range order, approximately the same in the two phases. On further decrease in the temperature the proportion of disordered phase decreases and finally disappears.

An analysis of the ratio of short-range to long-range order in $NbC_y$ showed[57] that the presence of the maximum possible amount of short-range order for the given composition is a necessary but not a sufficient condition for the appearance of long-range order. It follows that short-range and long-range order can be formed by different mechanisms in niobium carbide: only the long-range interactions (probably, the phonon subsystem) can account for the formation of long-range order, whereas short-range order may be caused

by interactions with a radius of action comparable with the interatomic distance (electronic subsystem).

NMR studies of non-stoichiometric vanadium compounds[79] also detected an effect of the interstitial C, N, and O atoms on the degree of short-range order and on the distribution of vacancies. In $VC_y$ and $VN_y$ the type of short-range order is determined by the mutual repulsion of the vacancies. The insertion of oxygen atoms into the crystal lattice of vanadium monocarbide produces a random distribution of vacancies in a mutually ordered arrangement of carbon and oxygen atoms in the resulting oxide carbide $VC_{0.5}O_{0.5}$. The insertion of hydrogen atoms into $VC_y$ and $VN_y$ does not affect the type of short-range order. Thus we may conclude from that work[79] that the interactions between vanadium atoms and their nearest neighbours are responsible for the formation of short-range order.

The above results (especially those of Ref. 57) show that compounds of variable composition prepared under different conditions can be structurally inhomogeneous. In other words, depending on the synthesis and heat treatment conditions the samples may contain regions in which the ordering differs in extent and in type, and the individual regions may

Table 1. Characteristics of the ordered phases formed in non-stoichiometric carbides, nitrides, and oxides and in their solid solution.

| Ordered phase | Type of lattice of the disordered basic phase | Non-metal content, at.% | $T_{stab}$, K | System | Lattice constants, A | Space group | Refs. |
|---|---|---|---|---|---|---|---|
| $Ti_6O$ | CPH | ~14.5 | 1090—1100 | H | — | — | [18—22] |
| $Ti_3O$ | CPH | ~25.0 | ~1670 | H | $a=5.1411$; $c=9.5334$ | | [23, 24] |
| $Ti_2O$ | CPH | ~33.3 | ~1270 | H | $a=2.9593$; $c=4.8454$ | $P\bar{3}m1$ | [23, 24] |
| $TiO_{0.7}$ | FCC | ~41.2 | 870—1260 | R | $a=a_0\sqrt{2}$; $b=3a_0/\sqrt{2}$ | — | [25, 26] |
| TiO | FCC | ~50.0 | ~1250 | M | $a=9.355$; $b=5.868$; $c=4.135$; $\gamma=107°32'$ | $A2/m$ | [27] |
| TiO | FCC | ~50.0 | 1250—1500 | C | $a=12.54$ | $Fm3m$, $F\bar{4}3m$ | [27] |
| $TiO_{1.20}$ | FCC | ~54.5 | ~1090 | R | $a=2.981$; $b=9.086$; $c=3.986$ | — | [27] |
| $TiO_{1.23}$ | FCC | ~55.6 | ~1050 | T | $a=6.642$; $c=4.156$ | — | [27] |
| $Zr_6O$ | CPH | ~14.3 | ~1070 | H | — | — | [28] |
| $ZrO_y$ | CPH | ~23.0 | ~710 | H | — | — | [29] |
| $Zr_3O$ | CPH | ~25.0 | 870—1070 | H | $a=5.5629$; $c=31.1850$ | $R\bar{3}2$ | [28] |
| $ZrO_x$ | CPH | 25.9—29.2 | ~770 | H | $a=a_0\sqrt{3}$; $c=c_0$ | $R\bar{3}_12$ | [30] |
| $Hf_6O$ | CPH | ~14.3 | ~1070 | H | — | — | [31] |
| $HfO_{1/6}$ | CPH | ~14.0 | ~690 | H | — | — | [29] |
| $Hf_3O$ | CPH | ~25.0 | ~1070 | H | — | — | [31] |
| $V_6O$ | BCC | ~12.5 | — | TC | $a=b=3.114$; $c=2.994$; $\alpha=\beta=90.3°$; $\gamma=90°$ | — | [32] |
| $\beta$-$V_4O$ | BCC | 16.0—20.0 | ≤2210 | T | $a=2.98$; $c=3.36$ | $I4/mmm$ | [33] |
| $\beta'$-$V_{16}O_3$ | BCC | 14.0—16.0 | ≤940 | T | $a=11.96$; $c=6.62$ | $I4/mmm$ | [33] |
| $\varepsilon$-$V_3O$ | BCC | 22.0—28.0 | ≤1640 | M | $a=16.68$; $b=16.50$; $c=17.60$; $\beta=90°20'$ | $P2_1/c$ | [33] |
| $\gamma$-$V_2O$ | BCC | 32.0—36.0 | ≤1730 | M | $a=32.47$; $b=20.49$; $c=20.56$; $\beta=129°40'$ | $C2/m$, $C2$ | [33] |
| $V_{52}O_{64}$ | FCC | 54.5—56.5 | ~870 | T | $a=11.72$; $c=8.245$ | — | [35] |
| $VO_{1.27}$ | FCC | ~56.0 | <1070 | T | $a=16.623$; $c=16.515$ | — | [34] |
| $Nb_6O$ | BCC | ~14.3 | 570—770 | T | $a=3.384$; $c=3.274$ | — | [36] |
| $Nb_4O$ | BCC | ~20.0 | 770—970 | T | $a=6.65$; $c=3.32$ | — | [37] |
| $Nb_2O$ | BCC | ~33.3 | 670—770 | T | $a=6.645$; $c=4.805$ | — | [36] |
| $NbO_2$ | H | ~66.6 | ~1520 | T | $a=13.71$; $c=5.985$ | $I4_1/a$ | [38] |
| $Ta_6O$ | BCC | ~14.3 | <770 | T | $a=3.363$; $c=3.254$ | — | [39, 40] |
| $Ta_4O$ | BCC | ~20.0 | <770 | R | $a=3.61$; $b=3.27$; $c=3.20$ | — | [39] |
| $Ta_2O$ | BCC | ~33.3 | >720 | T | $a=6.675$; $c=4.721$ | — | [39] |
| $\delta'$-$Ti_2N$ | T | ~33.3 | ~770 | T | $a=4.226$; $c=8.452$ | — | [41] |
| $\delta''$-$Ti_2N$ | T | ~37.0 | ≤1070 | T | $a=4.144$; $c=8.781$ | — | [42] |
| $\alpha$-V(N) | BCC | ~3.8 | ~570 | R | $a=12.52$; $b=12.10$; $c=2.988$ | — | [43] |
| $\beta$-V(N) | BCC | ~7.2 | ~1520 | T | $a=a_0\sqrt{2}$; $c=c_0$ | — | [39] |
| $\alpha'$-$V_8N$ | BCC | ~11.0 | — | T | $a=b=3.114$; $c=2.994$; $\alpha=\beta=90.5°$; $\gamma=90°$ | — | [32] |
| $\alpha''$-$V_8N$ | BCC | ~11.0 | — | T | $a=6.228\sqrt{2}$; $c=2.994$ | — | [32] |
| $\delta'$-$VN_y$ | FCC | 44.0—47.0 | ≤790 | T | $a=8.150$; $c=8.150$ | — | [44] |
| $\delta'$-$NbN_y$ | FCC | ~43.0 | ≤1670 | T | $a=4.382$; $c=8.632$ | $I4/mmm$ | [44] |
| $Ta_8N$ | BCC | ~11.1 | 580—650 | T | $a=b=4a_0$; $c=4.024a_0$ | — | [45] |
| $Ta_{38}N_5$ | BCC | ~11.6 | 580—650 | T | $a=b=6a_0$; $c=2.08a_0$ | — | [45] |
| $\delta$-$Ti_2C$ | FCC | 33.0—40.0 | ≤1470 | C | $a=8.634$ | $Fd\bar{3}m$ | [46] |
| $Ti_8C_5$ | FCC | 37.0—43.0 | ≤1370 | TG | $a=6.115$; $c=14.90$ | $R\bar{3}m$ | [44] |
| $\delta'$-$TiC_y$ | FCC | 34.2—41.5 | 670—1460 | C | $a=2a_0$ | $Fd\bar{3}m$ | [47] |
| $\delta'$-$ZrC_y$ | FCC | 39.0—43.0 | ≤1370 | TG | $a=6.630$; $c=16.26$ | — | [44] |
| $ZrC_y$ | FCC | 38.6—42.5 | 670—1470 | C | $a=2a_0$ | — | [47—49] |
| $\beta'$-$V_2C$ | CPH | ~33.0 | ~1800 | H | $a=4.997$; $c=4.658$ | — | [50] |
| $V_6C_5$ | FCC | ~45.5 | ~1370 | M | $a=5.09$; $b=10.81$; $c=8.81$; $\gamma=109°47'$ | — | [51] |
| $V_6C_5$ | FCC | ~45.5 | ≤1270 | TG | $a=5.09$; $c=14.40$ | $P\bar{3}_2$ | [52] |
| $\delta'$-$VC_y$ | FCC | ~46.6 | ≤1500 | C | $a=8.330$ | $P4_332$ | [44] |
| $\delta''$-$VC_y$ | FCC | 45.0—47.0 | ≤1520 | M | $a=a_0\sqrt{3/2}$; $b=a_0\sqrt{6}$; $c=3a_0/\sqrt{2}$; $\gamma=109°28'$ | — | [50] |
| $Nb_2C$ | CPH | ~33.3 | ≤1470 | R | $a=10.906$; $b=4.969$; $c=3.096$ | $Pnma$ | [53, 54] |
| $Nb_2C$ | CPH | ~33.3 | >1470 | H | $a=a_0\sqrt{3}$; $c=c_0$ | — | [53] |
| $Nb_4C_3$ | FCC | ~43.0 | — | C | $a=4.440$ | — | [55] |
| $Nb_6C_5$ | FCC | 42.8—45.5 | — | TG | — | — | [56] |
| $Nb_6C_5$ | FCC | 44.7—46.8 | ≤1370 | M | $a=c=5.4605$; $b=9.4579$; $\alpha=\gamma=90°$; $\beta=109.47°$ | $C2/m$ | [57, 58, 66] |
| $Ta_2C$ | CPH | ~33.3 | <1900 | H | $a=a_0$; $c=c_0$ | $P\bar{3}m1$ | [59] |
| $Ta_4C_3$ | FCC | ~43.0 | — | C | $a=4.42$ | — | [55] |
| $Ti_2CO$ | FCC | ~41.1 | — | C | $a=a=2a_0$ | $Fd\bar{3}m$ | [60] |
| $TiC_{0.5}O_{0.5}$ | FCC | — | — | C | $a=4.280$ | — | [61] |
| $TiC_xN_y$ | FCC | $x+y\leq 0.72$ | — | C | $a=2a_0$ | $Fd\bar{3}m$ | [48, 49, 62—64] |
| $ZrC_xN_y$ | FCC | $x+y\leq 0.74$ | — | C | $a=2a_0$ | $Fd\bar{3}m$ | [48, 49, 62—64] |
| $VC_{0.5}O_{0.5}$ | FCC | — | — | M | $a=8.28$; $b=4.14$; $c=4.20$; $\beta=90°41'$ | — | [65] |
| $VC_xN_y$ | FCC | 46.6 | 1300 | C | $a=2a_0$ | $P\bar{3}_112$ | [67] |
| $VC_xN_y$ | FCC | 45.5 | 1500 | TG | $a=a_0\sqrt{3/2}$; $c=2a_0/\sqrt{3}$ | — | [68] |

Symbols: C, cubic; T, tetragonal; H, hexagonal; TG, trigonal; R, rhombic; M, monoclinic; TC, triclinic; CPH, close-packed hexagonal; BCC, body-centred cubic; FCC, face-centred cubic; $a_0$, $b_0$, $c_0$ are the lattice constants of the disordered basic phase; $T_{stab}$ is the stability range of temperature.

be combined in different ways. The relative amount and size of the regions can also differ between samples. So far these effects in interstitial phases have tended to be ignored, in spite of the extensive data available on this problem in the case of metal alloys (see, for example, Ref.80). The type of structural inhomogeneity in the sample can have a marked influence on the physicochemical properties of the substance: these effects are often incorrectly attributed to electronic factors. In this sense establishing a state close to equilibrium becomes especially relevant to the solution of the fundamental problem in physicochemical analysis: the study of the composition–structure–property dependence.

Most of the alloys and solid solutions used in modern technology are in a hetero-phase state which gives them special physical properties: a high mechanical strength, hardness, and heat resistance, a low electrical conductivity, etc. Many structural and physical studies have shown that the properties of interstitial and of substitutional solid solutions are determined by the morphology, substructure, and nature of the conjugated phases. The required types of substructure are generated by using appropriate methods of heat treatment: quenching, annealing, etc.

Neutron diffraction, X-ray diffraction, and electron microscopic work has shown that hetero-phase structures are very diverse and differ in the shape of the inclusions and in their orientation relative to the crystallographic axes of the host crystal, as well as in their mutual disposition. In metal alloys we often find a periodicity (or a modulation) in the distribution of the inclusions: under these conditions the phase which is precipitated by the decomposition of the cubic (uniform) solid solution can have a similar or a lower symmetry. The periodicity of the distribution of inclusions can be so marked as to generate an additional diffraction pattern.

In terms of conventional thermodynamic considerations the shape of a crystal of the new phase can be related to its surface tension; this point of view suggests that the deposited crystals should be in the form of regular polyhedra. However, in studies of hard alloys based on interstitial phases (carbides, nitrides, carbide nitrides) it was found that the crystals of the new phase often consist of platelets or needles, whereas regular grids are formed by the precipitated phases in metallic alloys. On the other hand from the standpoint of classical thermodynamics as applied to phase transitions the free energy of a two-phase system depends on the total volume of each phase, but not on the relative position of the inclusions or on the area of their faces: it follows that the distribution of the inclusions should be random.

The special features of phase transitions in solids cannot be explained without allowing for the elastic stresses created during the transitions. The orientational relationships, the shape, and the mutual arrangement of the mother phase and of the precipitate are inexplicable otherwise. However, this approach has not so far been adequately explored in respect of non-stoichiometric compounds of the interstitial phase type. One of the few studies of the effect of the elastic deformation energy on the formation of solid solutions of carbides and nitrides[81] established a correlation between the elastic deformation energy, the decomposition temperature of the solid solution, and the possibility of developing short-range and long-range order. In particular it was shown that short-range order is observed in solid solutions of compounds of variable composition when the maximum energy of the elastic deformation is approximately 3–5 kJ mole$^{-1}$. Thus from a knowledge of the elastic deformation energy we can assess the extent of disturbance of the crystal lattice and the likely type of short-range order, and we can identify hidden regions for the decomposition of the solid solution, which strongly affect the physicochemical properties of these solutions.

## IV. FILLING OF STRUCTURAL VACANCIES IN COMPOUNDS OF VARIABLE COMPOSITION

Problems associated with the filling of structural vacancies in the crystal lattice of compounds of variable composition at high temperatures and pressures are of direct interest. The possibility was first suggested as a result of a study[82] of the monoxide $FeO_y$ at high temperature and pressure. It was later shown[83] that defect-free $FeO_y$ can be obtained by the simultaneous application of high pressure (7.74 GPa) and temperature (1920 K) to the material (which contained ~14% of vacancies in each sublattice in its initial state). Large increases in the density and in the lattice constant of the sample were observed. The partial or complete filling of the vacancies as a result of thermo-baric treatment has been observed also in other materials:[84–92] for example, in titanium and vanadium monoxides, in the oxide carbides of titanium, vanadium, and niobium, and in the oxide nitrides of titanium and vanadium (Table 2).

From the data listed in Table 2 we conclude that the vacancies can be filled only by the combined application of high temperature and pressure. Vacancies can be filled in either sublattice up to a predetermined threshold value, when all the sites in the sublattice are occupied by atoms of the appropriate kind and all the vacancies have disappeared. We should stress that vacancy filling is possible only under static loading conditions. Dynamic (shock) compression does not result in the disappearance of structural vacancies. The data in Table 2, like other published results,[84–92] suggest a definite sequence (in space and time) of processes stimulated by the thermo-baric treatment: in other words, they suggest a diffusion mechanism for the filling of vacancies.

The thermo-baric treatment produces not only vacancy filling but also a change in the state of charge of the atoms. This is shown by the fact that the X-ray emission spectra of the samples of composition $TiO_{0.88}$ and $TiO_{1.27}$ have a different shape[6,92] after the thermo-baric treatment (Table 2). The decrease in the concentration of structural vacancies and the change in the charge state of the atoms caused by the application of high temperature and pressure should produce marked changes in the properties of compounds of variable composition. It has long been assumed that the states established at high temperatures and pressures can be studied only under those conditions, because the state is not retained when the pressure is lowered to normal values.

We have shown[88] that the state induced by high temperature and pressure can be preserved indefinitely even under normal conditions: in this way the characteristics of a substance subjected to thermo-baric treatment can be investigated by conventional methods.

The changes in properties are clearly seen in the case of the monoxide $VO_{0.91}$.[93,94] After thermo-baric treatment the magnetic susceptibility (which initially obeyed the Curie–Weiss law) becomes temperature-independent; it also changes by a large amount.[94] A study of the effect of thermo-baric treatment on the electronic structure of $VO_{0.91}$ (by comparing calculations by the SCF MO LCAO method in the MWH approximation with X-ray emission spectra) showed that the change in the parameters of the electronic structure (electronic configuration of the atoms, effective charges, bond occupancies in nearest-neighbour atoms) varies monotonically with pressure. An increase in pressure changes the occupancy of the valency orbitals of vanadium towards the value for the neutral atom. This is confirmed by X-ray emission

data, which indicate, in particular, a decrease in the degree of $p-d$ hybridisation of the wave functions of the vanadium atoms.[93]

The use of high pressures and temperatures, especially in the case of compounds with structural vacancies in both sublattices, has helped to solve another important problem: the preparation of the so-called imaginary compounds whose existence had been predicted by Mendeleev.[95] A detailed discussion of this problem will be found in Refs. 88, 92, and 96–100: we shall only state that the imaginary chemical compound concept is one of the chemical methods of predicting not only the region of existence of compounds of variable composition but also the possibility of preparing new compounds.

Table 3. Conditions for the formation of the cubic carbides $V_2C$, $VC_{1.0}$, and $Nb_2C$.

| $T$, K | $V_2C$ (Ref. 108) | | $VC_{1.0}$ (Ref. 108) | | $Nb_2C$ (Ref. 102) | |
|---|---|---|---|---|---|---|
| | $\Delta G$, kcal mole$^{-1}$ | $p$, GPa | $\Delta G$, kcal mole$^{-1}$ | $p$, GPa | $\Delta G$, kcal mole$^{-1}$ | $p$, GPa |
| 700 | 0.97 | 43.6 | 4.5 | 92.3 | — | — |
| 1000 | 1.77 | 79.6 | 10 | 205.0 | 5.0 | 205.0 |
| 1300 | 2.04 | 92.7 | 19 | 389.5 | — | — |
| 2000 | — | — | — | — | 7.0 | 285.0 |
| 3000 | — | — | — | — | 11.0 | 450.0 |

The crystal-chemical conditions for the production of imaginary chemical compounds in interstitial phases have been formulated:[88,92,98–102] they state that thermo-baric treatment can be used to change the concentration of structural vacancies (up to the complete elimination of vacancies) in one or in two sublattices simultaneously with formation of a stoichiometric compound. Hence, it is pointed out[88,92,98–100] that the stability regions of the cubic carbides and nitrides of subgroup IVa–Va metals can be shifted as far as the compositions $M_2C$, $M_2N$ (lower limit) and $MC_{1.0}$, $MN_{1.0}$ (upper limit), which are not accessible under normal conditions. The most detailed thermodynamic treatment of this phenomenon will be found in Refs. 101 and 103–106. It has been used in calculations of the thermo-baric conditions of formation of stoichiometric, defect-free titanium monoxide,[103] and zirconium[101,104,106] and vanadium carbides.[105,106]

The writers,[102] using Leipunskii's method[107] in the quasi-one-component approximation, have calculated the formation conditions at high $p$ and $T$ (Table 3) of the cubic modification of the lower niobium carbide $Nb_2C$, which usually crystallises in the hexagonal system. The free energy difference $\Delta G$ between the hypothetical cubic carbide $Nb_2C$ and the hexagonal carbide obtained in practice was identified with the quantity $p\Delta V$, where $\Delta V$ is the change in volume of the crystal accompanying the transition between the two modifications (ignoring the baric compression and the thermal expansion of the crystal[102]). The same approach was later used[108] to calculate the conditions for the thermo-baric synthesis of the cubic (NaCl type) $V_2C$ and $VC_{1.0}$ carbides. As Table 3 shows, extreme values of $p$ and $T$ are needed to yield these compounds. The estimated pressures needed to give the cubic modifications of the carbides $Nb_2C$, $V_2C$, and $VC_{1.0}$ are probably too high because of the neglect[102,108] of baric and thermal effects. According to our calculations[105,106] the thermo-baric synthesis of the defect-free cubic vanadium carbide $VC_{1.0}$ at 700, 1000, and 1300 K requires pressures of 20, 27, and 37 GPa respectively, i.e. much lower than those given in Ref. 108. Nevertheless all theoretical estimates[101–106,108] of the effect of thermo-baric treatment on compounds

Table 2. Chemical composition, lattice constants ($a$), density ($\rho$), and number of formula units in the unit cell ($n$) of the monoxides, oxide carbides, and oxide nitrides of titanium and vanadium before (I) and after treatment at pressure $p$ and temperature $T$ for time $\tau$ (II).

| Composition | $a$, Å | | $\rho$, g cm$^{-3}$ | | $n$ | | Thermo-baric treatment condition | | | Refs. |
|---|---|---|---|---|---|---|---|---|---|---|
| | I | II | I | II | I | II | $p$, GPa | $T$, K | $\tau$, min | |
| $TiO_{0.88}$ | 4.1890 | 4.2107 | 4.93 | 5.50 | 3.52 | 4.01 | 9.0 | 1470 | 2 | [84] |
| $TiO_{1.27}$ | 4.1667 | 4.1742 | 4.79 | 4.90 | 3.06 | 3.15 | 9.0 | 1510 | 3 | [84] |
| $TiC_{0.44}O_{0.57}$ | 4.2910 | 4.3080 | 4.84 | 5.15 | 3.70 | 3.98 | 9.0 | 1470 | 1 | [85, 86] |
| $TiC_{0.22}O_{0.44}$ | 4.2416 | 4.2471 | 4.91 | 5.00 | 3.92 | 4.01 | 7.74 | 1970 | 5 | [90] |
| $TiC_{0.42}O_{0.44}$ | 4.2864 | 4.2909 | 4.82 | 4.90 | 3.81 | 3.92 | 7.74 | 1870 | 5 | [90] |
| $TiC_{0.30}O_{0.74}$ | 4.2571 | 4.2739 | 4.84 | 5.16 | 3.55 | 3.83 | 7.74 | 1870 | 5 | [90] |
| $TiC_{0.19}O_{0.81}$ | 4.2333 | 4.2566 | 4.87 | 5.22 | 3.52 | 3.84 | 7.74 | 1870 | 5 | [90] |
| $TiN_{0.37}O_{0.51}$ | 4.2270 | 4.2448 | 5.14 | 5.32 | 3.82 | 4.00 | 9.0 | 1670 | 2 | [85, 86] |
| $TiN_{0.45}O_{0.28}$ | 4.2260 | 4.2329 | 5.07 | 5.14 | 3.93 | 4.00 | 7.74 | 1270 | 5 | [89] |
| $TiN_{0.32}O_{0.40}$ | 4.2206 | 4.2260 | 5.07 | 5.10 | 3.91 | 3.96 | 9.0 | 1870 | 5 | [89] |
| $TiN_{0.22}O_{0.46}$ | 4.2110 | 4.2222 | 5.10 | 5.15 | 3.93 | 4.00 | 9.0 | 2070 | 5 | [89] |
| $VO_{0.91}$ | 4.0447 | 4.1203 | 5.70 | 6.21 | 3.48 | 4.00 | 9.0 | 1870 | 1.5 | [88] |
| $VO_{0.97}$ | 4.0574 | 4.1030 | 5.63 | 6.10 | 3.41 | 3.82 | 9.0 | 1870 | 1.5 | [88] |
| $VO_{1.01}$ | 4.0689 | 4.1073 | 5.62 | 5.90 | 3.40 | 3.67 | 9.0 | 1770 | 1.5 | [88] |
| $VO_{1.07}$ | 4.0874 | 4.1123 | 5.53 | 5.75 | 3.34 | 3.54 | 7.74 | 1670 | 2 | [88] |
| $VC_{0.62}O_{0.16}$ | 4.1307 | 4.1519 | 5.64 | 5.75 | 3.78 | 3.93 | 7.74 | 1670 | 7 | [87] |
| $VN_{0.56}O_{0.21}$ | 4.0820 | 4.0920 | 5.94 | 6.02 | 3.92 | 4.00 | 9.0 | 2070 | 1.5 | [91] |
| $VN_{0.57}O_{0.33}$ | 4.1100 | 4.1351 | 5.89 | 6.03 | 3.84 | 3.99 | 9.0 | 2070 | 1 | [91] |
| $VN_{0.46}O_{0.50}$ | 4.1161 | 4.1375 | 5.77 | 5.92 | 3.71 | 3.87 | 9.0 | 2070 | 1 | [91] |
| $VN_{0.51}O_{0.46}$ | 4.1203 | 4.1351 | 5.89 | 5.98 | 3.73 | 3.87 | 9.0 | 1870 | 2 | [91] |

of variable composition lead to the same conclusion: the concentration of vacancies can be lowered, and new modifications of the compounds can be produced, by using this treatment.

On the whole, both the experimental and the theoretical studies of compounds of variable composition under thermobaric conditions so far reported indicate the possibility (previously unknown) of controlling the properties of a substance only by changing the concentration of vacancies in the unit cell while retaining the initial composition and structure type.

## V. THERMODYNAMICS OF THE FORMATION OF STRUCTURAL VACANCIES

It is clear from the above discussion that structural vacancies should be distinguished from the point defects of the vacancy type usually discussed in the literature, which are formed either at high temperatures (thermal vacancies) or by irradiation (Frenkel defects).

In the description of point defects[109] the energy of formation of the vacancies ($E$) is assumed to be constant: under these conditions the change in the free energy of the crystal due to the formation of $n$ vacancies is

$$\Delta G = nE - T\Delta S \qquad (1)$$

where $\Delta S$ is the entropy change resulting from the addition of $n$ vacancies to the crystal. In the case of point defects the contribution of the vibrational component of the entropy to $\Delta S$ is assumed to be negligibly small (on the evidence of experimental data on thermal vacancies). Therefore the quantity $\Delta S$ is practically equal to the configurational component of the entropy, i.e.

$$\Delta S = k \ln \frac{N!}{n!\,(N-n)!} \qquad (2)$$

where $N$ is the number of sites in the crystal and $k$ is Boltzmann's constant.

By minimising the free energy and simplifying we can obtain from Eqns.(1) and (2) the following expression for the concentration of point defects of the thermal vacancy type:

$$c = \frac{n}{N} = \exp\left(-\frac{E}{kT}\right) \qquad (3)$$

The energy of formation of thermal vacancies in metal and metal-like compounds is $E \cong 1$ eV (for example, $E$ is 1.27, 1.10, and 0.95 eV in copper, silver, and gold respectively[110]). At room temperature this value of $E$ corresponds to a very low relative number of thermal vacancies ($c \cong 10^{-17}$), i.e. the average distance between thermal vacancies is of the order of a millimetre. At 2000 K the equilibrium relative number of vacancies becomes $c = 2 \times 10^{-3}$. Hence, as reported,[109] the equilibrium concentration of thermal vacancies in metals is negligibly small even near the melting point.

In compounds of the interstitial phase type such as transition metal carbides, nitrides, and oxides a high concentration of structural vacancies is a characteristic property, and the concept of point defects in these materials is almost meaningless.[111] Furthermore, in compounds of the interstitial phase type (for example, oxides) vacancies can exist in two sublattices at the same time (the non-metal and the metal sublattice); vacancies in the two sublattices have different effects on the properties of the compound.[112] Obivously, the vacancies in compounds of variable composition have a non-thermal origin, and their formation is closely related to the structural properties of the interstitial phase: these vacancies are therefore now called structural.

The presence of a large number of structural vacancies in compounds of variable composition has a marked effect on the vibrational entropy, which cannot be neglected in this case. The thermodynamic description of non-stoichiometric compounds allowing for the formation of structural vacancies[2,3,9,13,14,113–116] is based on the following considerations.

Consider a compound (in equilibrium at some temperature $T$) consisting of $i$ non-equivalent sublattices each containing $n_i$ vacancies and $N_i$ filled sites. The free energy $\Delta G(n)$ of such a crystal at constant pressure can be written[3]

$$\Delta G(n) = \Delta G + \sum \int_0^{n_i} \Delta H_i \, \mathrm{d}n_i - T\left(\Delta S_\kappa + \int_0^{n_i} \Delta S_i \, \mathrm{d}n_i\right) \qquad (4)$$

where $\Delta G = \Delta H - T\Delta S$ is the free energy of the defect-free crystal, $\Delta H$ is the heat of formation of the defect-free crystal, $\Delta S$ is the change in entropy accompanying the formation of the defect-free crystal, $\Delta H_i$ is the energy of formation of the structural vacancies in the $i$-th sublattice of the crystal, $\Delta S_i$ is the change in vibrational entropy due to the formation of vacancies in the $i$-th sublattice, and

$$\Delta S_\kappa = k \sum \ln[(N_i + n_i)!/N_i! n_i!]$$

is the change in the configurational component of the entropy on formation of the vacancies.

It follows from (4) that the heat of formation of a crystal containing structural vacancies is

$$\Delta H(n) = \Delta H + \sum \int_0^{n_i} \Delta H_i \, \mathrm{d}n_i \qquad (5)$$

and the entropy change is

$$\Delta S(n) = \Delta S + \Delta S_\kappa + \sum \int_0^{n_i} \Delta S_i \, \mathrm{d}n_i \qquad (6)$$

Eqn.(4) can therefore be written in terms of the free energy of formation of the structural vacancies:

$$\Delta G_i = \Delta H_i - T\Delta S_i \qquad (7)$$

In general Eqn.(4) assumes a dependence of $\Delta H_i$ and $\Delta S_i$ on the concentration of structural vacancies, i.e. it assumes interactions between the vacancies. Assuming that $\Delta S_i$ is negligibly small and that no interaction takes place between the vacancies (i.e. adopting the weak defect interaction approximation) gives a change in the energy of formation of vacancies proportional to their number, so that Eqn.(4) reduces to Eqn.(2). Thus formula (2) is a special case of Eqn.(4) which can be used to describe the behaviour of both structural vacancies and point defects; the parameters of this description are the quantities $\Delta H_i$ and $\Delta S_i$.

On reaching the equilibrium vacancy concentration for the given temperature $c_i = n_i/N_i$ the free energy $\Delta G(n)$ goes through a minimum, i.e. $\partial \Delta G(n)/\partial n_i = 0$. Using this condition in conjunction with the Stirling formula for the series expansion of $\Delta S_i$ we obtain from (4), after simplification, an expression relating the equilibrium concentration of structural vacancies in the $i$-th sublattice to their energy of formation and to the vibrational component of the entropy:

$$kT \ln c_i = -\Delta H_i + T \cdot \Delta S_i \qquad (8)$$

It follows from (8) that at any temperature above the absolute zero the vacancies are thermodynamically stable and their concentration can be decreased indefinitely but not brought to zero. Furthermore, if $\Delta H_i$ and $\Delta S_i$ are constant and independent of the number of structural vacancies we can expect a linear relationship between $\ln c_i$ and $T^{-1}$.

Data on the congruent evaporation of titanium and zirconium nitrides have been used[117,118] to determine the energies of formation of structural vacancies in the nitrogen sublattice

of these compounds on the assumption that vacancy interactions are negligible: the result (expressed for one molecule) was 0.94 ± 0.32 and 1.13 ± 0.06 eV respectively. The change in the vibrational component of the entropy caused by the formation of vacancies in zirconium nitride was found[118] to be $(0.31 \pm 0.04) \times 10^{-3}$ eV $K^{-1}$. However, the calculation[118] of the heat of formation $\Delta H^{\circ}_{298}$ and of the free energy of formation $\Delta G^{\circ}_{298}$ of zirconium nitride in its homogeneity region from the observed energies of formation and vibrational entropy changes of the structural vacancies gave a discrepancy between experiment and calculation increasing with the number of nitrogen vacancies and reaching 25% at the lower boundary of the homogeneity region. The discrepancy was attributed[118] to the neglect of the concentration dependence of the energy of formation of the vacancies. A comparison of experimental and calculated values of the activity of carbon in the homogeneity region of zirconium carbide similarly led to the conclusion[119] that satisfactory agreement between experiment and calculation is obtained only by allowing for the dependence of the energy of formation of the vacancies on the composition of the compound.

A detailed analysis[13,14,115] of existing experimental data on the congruent evaporation of a series of carbides and nitrides with a structure of the NaCl type has shown that the dependence of ln c on $T^{-1}$ is non-linear, and therefore that a change in defect density in these materials affects either the energy of formation of the vacancies, or the vibrational component of the entropy, or both, i.e. that vacancy interactions are present.

In compounds of variable composition with an NaCl type structure each metal atom is octahedrally surrounded by six sites of the non-metal sublattice which form the first coordination sphere; the second coordination sphere consists of twelve metal atoms. Let us consider a compound containing structural vacancies in only one of the sublattices (for example, the non-metal sublattice). We shall assume that the interaction between the non-metal atoms is limited to the first coordination sphere. When all the sites in the non-metal sublattice are filled the energy of formation of the vacancies will be denoted by $\Delta H_1$, and the vibrational component of the entropy by $\Delta S_1$. If all the sites of the non-metal sublattice adjacent to a given non-metal atom are vacant we shall use the symbols $\Delta H_2$ and $\Delta S_2$. In general, when some of the sites are occupied by non-metal atoms but some ($n$) are vacant, the energy of formation of the vacancies can be expressed as the sum

$$\Delta H_n = (1-n)\Delta H_1 + n\Delta H_2 \qquad (9)$$

Similarly, we can write for the vibrational component of the entropy

$$\Delta S_n = (1-n)\Delta S_1 + n\Delta S_2 \qquad (10)$$

If only the vibrational component of the entropy increases with the defect density, by inserting (10) into (4) and solving the resulting equation we obtain an expression for the equilibrium concentration of vacancies which allows for the dependence of $\Delta S_B$ on the number of vacancies in the homogeneity region of the compound:

$$kT \ln c_i = (1-n)T\Delta S_1 + nT\Delta S_2 - \Delta H \qquad (11)$$

If only the energy of formation of the vacancies $\Delta H_B$ varies with the number of defects the corresponding expression is

$$kT \ln c_i = T\Delta S - (1-n)\Delta H_1 - n\Delta H_2 \qquad (12)$$

Lastly, if both $\Delta H$ and $\Delta S$ are dependent on the defect density we have

$$kT \ln c_i = (1-n)T\Delta S_1 + nT\Delta S_2 - (1-n)\Delta H_1 - n\Delta H_2 \qquad (13)$$

Eqns.(11)–(13) assume the existence of a self-consistent solution for the equilibrium concentration of vacancies $c_i$ at a given temperature $T$ for known values of the parameters $\Delta H_{1,2}$ and $\Delta S_{1,2}$.

Thus even allowing for interactions only in the non-metal sublattice and assuming a simple linear dependence implies considering three types of solution and determining which of these solutions best describes the experimental data.

The quantities $\Delta H_1$, $\Delta H_2$, and $\Delta S_1$, $\Delta S_2$, have been determined,[13,14,115] and their statistical significance in describing the equilibrium concentration of structural vacancies in titanium, zirconium, and niobium carbides and nitrides by Eqns.(11)–(13) has been assessed by using the Fisher criterion, $F$.[120] By comparing the dispersion obtained for each of these equations with the $F$ criterion we obtain a statistical proof of the dependence of the energy of formation of vacancies and of the vibrational component of the entropy on the defect density of the compound; this suggests the presence of interactions between the vacancies, in keeping with earlier data.[57,76,68,79] An analysis of these results[13,14,115] also showed that the allowance for the dependence of the vibrational component of the entropy on the number of structural vacancies is more important than the corresponding correction for the energy of formation of the vacancies. As the defect density increases, the energy of formation of vacancies $\Delta H_B$ in the carbides and nitrides of titanium, zirconium, and niobium decreases (Table 4), denoting the presence of mutual repulsion between the vacancies.

Table 4. Energies of formation of structural vacancies $\Delta H_B$ and changes in the vibrational component of the entropy $\Delta S_B$ in the formation of structural vacancies in non-stoichiometric compounds.

| Compound | $\Delta H_B$, eV | $10^3 \Delta S_B$, eV $K^{-1}$ | Refs. |
|---|---|---|---|
| $ZrC_{1-n}$ | 0.524—0.520$n$ | 0,009—0.318$n$ | [13, 115] |
| $VC_{1-n}$ | 0.150 | 0,010 | [3] |
| $NbC_{1-n}$ | 0.532—0.411$n$ | —0,002—0,089$n$ | [115] |
| $TiN_{1-n}$ | 1.347—0.401$n$ | 0,415—0.241$n$ | [14] |
| $ZrN_{1-n}$ | 1.867—0.614$n$ | 0,726—0.462$n$ | [13,14] |

The quantities $\Delta H_B$ and $\Delta S_B$ for vanadium carbide were determined[3] in the approximation of non-interacting atoms, because the precision of the experimental data on the heat of formation of vanadium carbide was insufficient to determine the dependence of the energy of formation of the vacancies and of the vibrational entropy on the number of vacancies. The temperature dependence of the free energy of formation of the vacancies in the carbon sublattice for the vanadium carbide $VC_y$ (for one formula unit of the compound) was found to be[3]

$$\Delta G, \text{ eV} = 0.415 + 1.574 \cdot 10^{-3} T + 7.553 \cdot 10^{-8} T^2 - 0.17 \lg T - 0.458 \cdot 10^{-3} T \lg T + 4.522\, T^{-1}$$

In compounds with defects in both sublattices, such as the cubic modifications of titanium and vanadium monoxides, for which congruent evaporation data are not available, the energy of formation of the structural vacancies can be calculated by using Eqn.(5). An attempt to calculate the energy of formation of vacancies in titanium monoxide has been reported.[121] However, no attempt was made to evaluate

the precision of the experimental data on the heat of formation of $TiO_y$ in the homogeneity region, and as a result the form of the dependence of the energy of formation of the vacancies on the defect density of the metal and of the oxygen sublattice was incorrectly chosen; the results[121] cannot therefore be treated as reliable. In Refs.2 and 116 the energies of formation of the metal and the oxygen vacancies in $TiO_y$ and $VO_y$ are calculated by using the methods of mathematical statistics to allow for the precision of the experimental data, giving more meaningful results.

It follows from Eqn.(5) that the heat of formation of the crystal containing defects ($\Delta H(n)$) can be expressed in terms of the heat of formation of the defect-free crystal ($\Delta H$) and the energy of formation of vacancies in each of the sublattices. For the monoxides of vanadium and titanium (compounds with a double set of defects) we have

$$\Delta H(n) = \Delta H + \int \Delta H_M \, d n_M + \int \Delta H_O \, d n_O \qquad (14)$$

where $\Delta H_M$ and $\Delta H_O$ are the energies of formation of vacancies in the metal and the oxygen sublattice respectively.

The form of the dependence of $\Delta H_M$ and $\Delta H_O$ on the composition of the compound is not known, but these quantities can be determined by using existing experimental data on the composition dependence of the heats of formation in the homogeneity regions of titanium and vanadium monoxides[111,122] in conjunction with structural data[23,123] for these compounds. In the zeroth approximation we assume that the energy of formation of the vacancies is independent of the composition of the compound: this gives

$$\Delta H(n) = \Delta H + \Delta H_M n_M + \Delta H_O n_O \qquad (15)$$

According to (15) the heats of formation of the monoxides should be directly proportional to the numbers of defects in the metal and in the oxygen sublattice. However, it has been shown experimentally that the dependences deviate from linearity and have a point of inflection near the equiatomic composition.[111,112] The deviations may be due to experimental error, or to the dependence of the interatomic bond energy on the composition of the monoxides, resulting in a change in the energy of formation of the vacancies in the homogeneity region of the compound.

To allow for possible interatomic interactions we shall assume that $\Delta H_M$ depends on the interaction between metal atoms and $\Delta H_O$ on the interaction between oxygen atoms in the first coordination spheres of the metal and oxygen atoms respectively. Let $\Delta H_{M_1}$ and $\Delta H_{O_1}$ be the energies of formation of vacancies in the metal and in the oxygen sublattice in the perfect (defect-free) lattice of the monoxide, and let $\Delta H_{M_2}$ and $\Delta H_{O_2}$ be the energies of formation of vacancies in the metal and the oxygen sublattice when all the sites in the metal or the oxygen sublattice adjacent to the given metal or oxygen atom are vacant. In general, when only some of the lattice sites are occupied by metal or oxygen atoms, the energy of formation of metal and oxygen vacancies can be expressed as (as was done for the carbides and the nitrides) as a sum of the products of $\Delta H_{M_1}$ and $\Delta H_{M_2}$ (or $\Delta H_{O_1}$ and $\Delta H_{O_2}$) by the fractional number of filled and of empty sites in the metal (or in the oxygen) sublattice:

$$\Delta H_M = (1-n_M)\Delta H_{M_1} + n_M \Delta H_{M_2};$$
$$\Delta H_O = (1-n_O)\Delta H_{O_1} + n_O \Delta H_{O_2}$$

Allowing for the nature of the dependence of $\Delta H_M$ and $\Delta H_O$ on the concentration of vacancies, four variants of the description of the heat of formation of a crystal containing defects in terms of the energy of formation of the vacancies in each of the sublattices are possible. According to (14) these variants correspond to the following cases: 1) the energies of formation of vacancies $\Delta H_M$ and $\Delta H_O$ are constant and independent of the vacancy concentration; 2) only $\Delta H_M$ varies with the concentration of vacancies, whereas $\Delta H_O$ stays constant; 3) $\Delta H_O$ varies, and $\Delta H_M$ stays constant; 4) $\Delta H_M$ and $\Delta H_O$ vary simultaneously. The Fisher criterion $F$ has been used[2,116] to identify which of these four assumptions has the highest probability, i.e. gives the best description of existing experimental data allowing for their precision. By comparing the dispersion with the value of the $F$ criterion it was shown that in the case of titanium monoxide the energies of formation of the vacancies in both sublattices are dependent on the concentration of the appropriate defects. Clearly, a similar dependence can be expected in vanadium monoxide, but the precision of the experimental data[112] on the heat of formation of $VO_y$ in the homogeneity region is too low to establish this fact unambiguously. The energies of formation of structural vacancies in the metal and the oxygen sublattice of titanium monoxide $TiO_y$ are $\Delta H_M$, eV $= -15.104 - 1.225\, n_M$ and $\Delta H_O$, eV $= -2.068 + 12.678\, n_O$ respectively.[116] For the vanadium monoxide $VO_y$ the energy of formation of vacancies in the metal and in the oxygen sublattice is $\Delta H_M = 5.32$ eV and $\Delta H_O = 8.172$ eV respectively.[2]

Thus by treating structural vacancies as analogues of interstitial atoms we can describe non-stoichiometric compounds in terms of a simple thermodynamic model. The change in the energy of formation of vacancies in the homogeneity regions of these compounds allows us to identify the nature of the interatomic interactions. Knowing the energy of formation of structural vacancies in the carbides, nitrides, and oxides of the transition metals we can calculate the synthesis conditions of the defect-free compounds.[101,104-106]

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The above discussion shows that structural vacancies in compounds of variable composition can be treated as analogues of interstitial atoms: for example, the deviation from stoichiometry can be wholly described as the formation in the nonmetal sublattice of a substitutional solution whose components are interstitial atoms and structural vacancies. Evidently, the defect state of the crystalline structure, i.e. the presence of a high concentration of structural vacancies, is the most important property of compounds of variable composition of the interstitial phase type.

The presence of a large number of structural vacancies offers some additional flexibility in the controlled synthesis of compounds of variable composition having prescribed properties. One possibility is to use a thermo-baric treatment to vary the vacancy concentration while preserving the initial composition and structure of the compound. Another means of fine control of all the properties of a compound of variable composition relies on the redistribution of the interstitial atoms and vacancies over the sites of the nonmetal sublattice. The study of vacancy distributions is of direct scientific interest because it offers a key to an understanding of the nature of interatomic interactions in compounds of variable composition. This is because the rearrangement of atoms and vacancies in a crystal lattice is a manifestation of interactions at the atomic level. So far the effect of the nature of the vacancy distribution on the properties of non-stoichiometric compounds has not been adequately studied, but we consider this approach to be very promising from a practical as well as a scientific aspect.

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# The Physicochemical Properties of Ionomer-containing Interpenetrating Polymer Networks

Yu.S.Lipatov and L.M.Sergeeva

The physicochemical properties of interpenetrating polymer networks of a new type, containing an ionomer as one of the components, have been examined. The results of the study of the morphology, viscoelastic properties, mechanical strength characteristics, and adhesive properties have been described. Data on the thermodynamic compatibility of the components in the systems studied have been given.
The bibliography contains 78 references.

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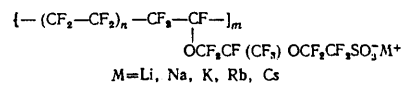
## I. INTRODUCTION

In recent years, an increasing number of papers have been published on the synthesis and study of the properties of interpenetrating polymer networks (IPN) and materials based on them.[1-4] This is due to the fact that, in addition to traditional binders for composite polymer materials, increasing use is now being made of complex binders consisting of components of different chemical character, which are second-generation binders, or hybrid binders.[5] A characteristic feature of hybrid binders is that after setting, they themselves are composite polymer materials, since as a consequence of the thermodynamic incompatibility of the components, setting is accompanied by the separation of microphase particles of one of the components, which can be regarded as the filler, distributed in a matrix of the other component.

Interpenetrating polymer networks are typical representatives of hybrid binders, whose use makes it possible to achieve much more complex combinations of different polymer structural states in composite materials, providing extensive possibilities for controlling the properties by the action of the filler.

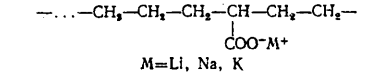
A number of papers[6-15] describe the study of a new type of interpenetrating polymer network, namely systems in which one of the components is an ionomer. Ionomers have been studied particularly intensively in the last 10–15 years. The term ionomer was previously used to describe only copolymers of α-alkenes with unsaturated mono- and dicarboxylic acids, in which some of the acidic groups were neutralised by metal ions.[16] The term ionomer now covers a wider range of polymers. Thus according to one definition,[5] ionomers are polymers whose chains contain a small quantity of ionogenic groups, usually not more than 10 mole %, so that the hydrocarbon chain is the main component, in contrast to poly-electrolytes, which have a high density of ionogenic groups in the chain. Other definitions of the term ionomer have been given; for example, ionomers have been defined[10] as ion-containing polymers in which the concentration of ionogenic groups is insufficient to ensure their solubility in water.

Ionomers based on polymers of different classes have been obtained. For example, fluorinated ionomers with the following structure have been prepared:[17]



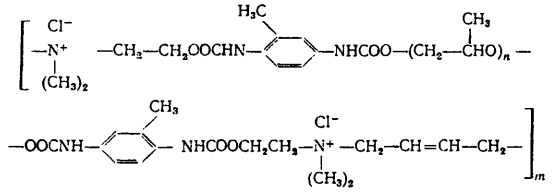
M=Li, Na, K, Rb, Cs

The structural formula of an ionomer based on ethylene and acrylic acid[18] is:



M=Li, Na, K

Ionomers with quaternary nitrogen atoms in the main chain are often called ionenes.[19] For example, a polyurethane ionene based a glycol oligoether, tolylene di-isocyanate (TDI), 2-dimethylaminoethanol, and 1,4-dichlorobut-2-ene has the following structural formula:[19]



The good operational characteristics of ionomers and the possibility of using them in various branches of technology have led to a considerable increase in studies of their synthesis and properties.

Theoretical ideas on the structure of ionomers are being developed by Eisenberg.[12,13,20,21] According to his ideas, the thermodynamic incompatibility of the salt groups and the polymer matrix, and the electrostatic interaction of the ionogenic groups, lead to the formation of multiplets and clusters. Multiplets consist exclusively of ionogenic groups, and contain a maximum of 8–10 ion pairs; clusters consist of multiplets separated by polymer chains, that is clusters contain both ionogenic groups and polymer chains. According to Eisenberg, cluster formation is observed in ionomers when a certain critical concentration of ionogenic groups in the chains has been reached. This is consistent with ideas on microphase separation in block copolymers and other multicomponent systems where the blocks are thermodynamically incompatible. Experimental studies of various ionomers based on ethylene, styrene, ethyl acrylate, etc.

by electron microscopy, neutron scattering, X-ray diffraction, and infrared spectroscopy[6,20,23] confirm Eisenberg's view that aggregates of two types, multiplets and clusters, exist. This explains the sharp change in a range of physicomechanical and thermophysical properties, such as the viscosity of the melt, the glass-transition temperature $T_g$, the modulus of elasticity, and the dynamic mechanical characteristics, when ionogenic groups are introduced into polymer chains.

A number of comparatively recent papers[10,11,15,24-30] describe the study of the properties of polyurethane ionomers. Polyurethanes show microphase separation at the level of the flexible and rigid blocks, leading to the formation of systems with a high level of heterogeneity.[22] Moreover, in addition to a chemical bond network, these polymers contain a network of physical bonds, which determines to a large extent the properties of materials based on polyurethanes.[31] The introduction of ionogenic groups into polyurethanes creates an additional, "ionic", network, which has a considerable influence on a range of properties of these systems.

The data obtained to date in the study of the properties of polyurethane ionomers are not unambiguous. On the one hand, in a series of papers[25-28] on the study of segmented polyurethanes in the ionic form by infrared spectroscopy, it was concluded that in these materials the network of hydrogen bonds is broken down, and that hydrogen bonds of a new type are formed, leading to a rearrangement of the segments of the polymer chain and to disordering of the rigid domains; it was also concluded that there is a deterioration in the conditions for self-association of the urethane groups, contrary to the previously proposed[32] scheme based on an increase in the self-association of the urethane groups and the segregation in polyurethane ionomers. On the other hand, other data indicate an increase in the segregation of the blocks of different chemical character when ionic centres are introduced into polyurethanes.[29] An increase in micro-phase separation is assumed to be responsible for the decrease in $T_g$ for the flexible blocks in polyester–polyurethane ionomers, compared with non-ionogenic polyurethanes.[30] The ambiguity in the conclusions about the influence of ionogenic groups on the structure of polyurethane ionomers indicates a need for systematic studies in this field.

The combination of ionomers with polymers with a three-dimensional structure, leading to the formation of ionomer-containing IPN, is a promising method of obtaining new types of composite polymer materials. At the same time, the production of these complex systems unavoidably complicates the structure of the materials by changing the nature of the microphase separation, and hence influences the final properties of the materials. Studies published up to the present on ionomer-containing IPN are examined in the present review.

## II. MORPHOLOGY AND STRUCTURE

The determination of the influence of ionogenic groups on the morphology and structure of ionomer-containing IPN is of decisive importance.

A large proportion of the structural studies of IPN containing ionogenic groups, as for IPN of other types, has been carried out by electron microscopy. An electron-microscope study of IPN based on sulphonated cross-linked polystyrene (PS) and polyvinylpyridine (PVP) (see Fig.1) showed that the specimens of all the compositions studied had a cellular structure, indicating phase separation in the IPN.[33,34] When its concentration is high, the sulphonated PS forms a continuous phase with quaternised PVP distributed in it as inclusions with dimensions of 60–80 nm (Fig.1*a*). The size of the PVP domains decreases from 60–80 nm to 30–40 nm on going from specimens with a higher PS concentration to IPN specimens with a component ratio of 1:1 (Figs.1*b* and 1*c*). At medium compositions (Fig.1*c*), both phases are continuous, and with further decrease in the PS concentration, PVP becomes the continuous phase (Fig.1*d*). In this case the size of the PS domains is 10–20 nm. Inversion of the phases takes place with change in the PS/PVP ratio from 1:1 to 1:4.

Thus the ionomeric IPN examined above, like non-ionomeric IPN, have a cellular structure, but in some cases this structure is not clearly defined, possibly due[33] to some mixing of the two components of the IPN at the molecular level. The chief difference between the morphology of the ionomer-containing IPN being considered and ordinary IPN, however, is that analysis of the photomicrographs of IPN specimens with different compositions has shown that in addition to phase separation of the individual components in the IPN, in the ionomeric components themselves there is additional separation with the production of regions with a higher concentration of ionogenic groups.[33] Thus systems of this type will be provisionally four-phase systems, and not two-phase systems like ordinary IPN.

For IPN based on sulphonated PS and quaternised PVP, the size of the domains obtained experimentally was compared with that calculated using Donatelli's equation:[35,36]

$$D_2 = \frac{2\gamma W_2}{RT\nu_1[1/(1-W_2)-1/2]}$$

where $D_2$ is the size of the domains of component 2, forming inclusions in component 1, $W_2$ the weight fraction of component 2, $\gamma$ the interphase tension between the components of the IPN, $\nu_1$ the density of cross-linking of component 1, $R$ the universal gas constant, and $T$ the temperature. Comparison of the experimental and calculated values of $D_2$ in relation to the component ratio showed good agreement between theory and experiment only at a PVP concentration of 50% and above. At low PVP concentrations, the theoretical and experimental values differ considerably.

The introduction of ionogenic groups into one of the components of an IPN makes it possible to change the morphology and hence the mechanical properties of materials on thermal treatment. This was shown in a study of the influence of annealing on the morphology of IPN based on a triple copolymer of butadiene, styrene, and methacrylic acid (polymer 1) and a copolymer of styrene with divinylbenzene (polymer 2).[37] Polymer 1 was obtained in both the acidic form and the salt form. In the last case, films of polymer in the acidic form were treated with a 10% solution of sodium or caesium hydroxide; after this treatment, the polymer no longer dissolved in organic solvents, but only swelled, indicating the formation of an elastomer "cross-linked" by physical bonds. Only IPN specimens with medium compositions, with a component ratio of 1:1, were studied. The materials were treated by the method described above, except that to obtain contrast the specimens were treated with osmium tetroxide. Analysis of the electron-microscope photographs showed that in the original IPN the ionomeric component in the acidic form gives a continuous phase, with domains of the copolymer of styrene and divinylbenzene with dimensions of 10–13 nm distributed in it; a small quantity of domains with dimensions up to 70 nm is also present. On annealing (in this case thermal treatment at 110 °C for 24 h), both components of the IPN form continuous phases. When the ionomeric component is in the salt form, annealing gives the same effect, but to a lesser

degree. The observed phenomena are related to the fact that the ionic "cross-linkages", which are thermally labile, become weaker and undergo rearrangement on prolonged thermal treatment, leading to a change in the structure of the IPN and hence to a change in the physicomechanical properties.[37]

This possibility of rearranging ionic "cross-linkages" by thermal treatment has led to the production of thermoplastic IPN in which both components (one of which is an ionomer) are "cross-linked" by physical bonds.[38] One IPN of this type consists of a system based on a triple copolymer of styrene, ethylene, and butene (polymer 1) and an ionomer obtained by the copolymerisation of styrene, methacrylic acid, and isoprene (volume ratio of the components 90 : 10 : 1), followed by neutralisation of the COOH groups with an aqueous solution of NaOH or CsOH (polymer 2).[39,40,41,42] The triple copolymer, in the molecules of which the terminal styrene blocks are physical "cross-linkages", is a thermoplastic elastomer. In the ionomer, the ionogenic groups form domains which are also nodes of the physical network, so that at room temperature the ionomer behaves as a cross-linked polymer, and at high temperatures, as a result of the breakdown of the domains, flow of the material takes place, that is the ionomer behaves as a linear polymer.

Two methods can be used to obtain thermoplastic IPN. In the first method, polymers 1 and 2 are synthesised separately, after which they are blended in the molten state. These are mechanically blended thermoplastic IPN (MBT IPN). In the second method, the IPN are obtained by polymerising polymer 2 in a common solution in the presence of the previously prepared polymer 1. These are chemically blended thermoplastic IPN (CBT IPN). Thus thermoplastic IPN are materials intermediate between IPN and blends of thermodynamically incompatible polymers. The study of the morphology of these materials has revealed certain characteristic features.

Analysis of electron-microscope photographs of IPN specimens with a component ratio of 1 : 1 has shown[40] that when the acidic form of polymer 2 is used in CBT IPN, polymer 2 is the continuous phase. At 100% neutralisation of the methacrylic acid fragments, inversion of the phases is observed; polymer 1 becomes the continuous phase, and polymer 2 (the ionomer) is distributed in it as globules with dimensions of 100–200 nm. At a lower degree of neutralisation (15% and 20%), partial inversion is observed; there are regions in which both phases (polymers 1 and 2) are continuous. The structure of the mechanically blended thermoplastic IPN (MBT IPN) differs slightly from that examined above for the CBT IPN.[41] Thus in the case of the acidic form of polymer 2, although it is the continuous phase with domains of polymer 1 distributed in it (size of the domains 50–150 nm), the degree of blending is less than for the CBT IPN. Here also, inversion of the phases takes place on complete neutralisation, but the dimensions of the domains of polymer 2 show extensive scatter, from 500 nm to 2000 nm with a small quantity of even smaller domains (400–100 nm).

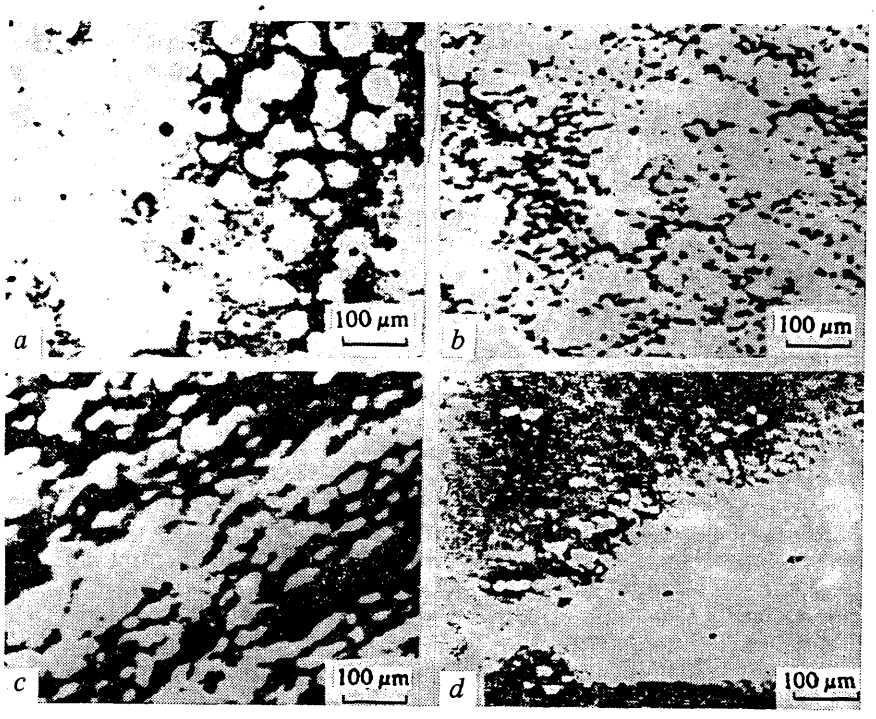



**Figure 1.** Photomicrographs of ionomer-containing IPN based on cross-linked polystyrene and polyvinylpyridine; PS/PVP ratio: *a*) 76/24, *b*) 58/48, *c*) 50/50, *d*) 20/80.[33]

Individual "islets" of polymer 2 consist of cells with domains of polymer 1 disseminated in them.

The change in the degree of phase continuity with increase in the degree of neutralisation of the polymethacrylic acid fragments in polymer 2 is an important characteristic of thermoplastic IPN. These changes in structure on going from the acidic to the salt form have been attributed[39-41] to a change in the viscosity of melts of these forms of polymer 2, which has been demonstrated experimentally.[39] The polymer with the lower viscosity, for example polymer 2 in the acidic form, generally tended to become the continuous phase. Increase in the degree of neutralisation led to an increase in the viscosity of the melt of polymer 2, and it became the dispersed phase. The component ratio naturally also has a significant influence on the phase continuity in IPN.

The morphological data for the CBT IPN studied were used to construct a generalised "phase continuity" diagram,[39] characterising the change in the degree of continuity with change in the component ratio in the IPN and degree of neutralisation of the groups of polymer 2.

For many CBT IPN compositions, inversion of the phases, although observed, ofter remains incomplete, that is there is to some extent continuity of both phases, attributed to the fact that the viscosities of the melts of the two polymers in the IPN are approximately equal.[39]

Thus study of the morphology of thermoplastic ionomer-containing IPN has shown that, like ordinary IPN, they have a high degree of heterogeneity, but (particularly CBT IPN) they have a finer structure than ordinary IPN, with smaller domain dimensions than in ordinary IPN and polymer blends. Moreover, the structure of these IPN can be varied over a wide range by varying the concentration of salt groups in the ionomer.

Small-angle X-ray scattering gives more complete information on the polymer structure than electron microscopy; in particular, it makes it possible to determine the size of the heterogeneous inclusions in the range 1–100 nm and other characteristics of the heterogeneity in amorphous systems. This estimation has been carried out for IPN based on the non-ionic form of network polyurethane and a polyurethane ionomer.[43] The ionomer was obtained from polyoxypropylene glycol, 2,4-tolylene di-isocyanate (TDI), 2-dimethylamino-ethanol, and 1,5-dibromopentane.

Analysis of the large-angle diffraction patterns of the individual polymers making up the IPN showed that they are typical amorphous polymers with a more or less developed heterogeneity, resulting from the segregation of the rigid and flexible blocks in the polyurethanes.[22] The degree of segregation can be estimated quantitatively by comparing the theoretical value of the mean-square fluctuation of the electron density $\Delta\bar{\rho}_c^2$ and the mean square fluctuation of the electron density of the real system studied $\Delta\bar{\rho}^2$; the parameter $\alpha = \Delta\bar{\rho}^{2\prime}/\Delta\bar{\rho}_c^2$ is introduced.[22] The quantity $\Delta\bar{\rho}_c^2$ characterises a so-called "ideal" two-phase system in which the micro-regions have the densities of the pure components, and the thickness of the interphase layer tends to zero. The value of $\Delta\bar{\rho}^{2\prime}$ depends both on the electron density of the components and on their degree of segregation in the system. The results of calculations of $\alpha$, $\Delta\bar{\rho}^{2\prime}$, and $\Delta\bar{\rho}_c^2$ for the individual networks (the non-ionic form of polyurethane and the polyurethane ionomer) showed that the $\Delta\bar{\rho}_c^2$ values differ little; at the same time, $\Delta\bar{\rho}^{2\prime}$ for polyurethane is 100 times that for the ionomer. Correspondingly, the degree of segregation $\alpha$ for polyurethane is 8 times that for the ionomer. Thus the results indicate that the original networks deviate considerably from the ideal two-phase structure.

The large-angle diffraction patterns showed that the interpenetrating polymer networks based on polyurethane and a polyurethane ionomer are also amorphous polymers. The results of the small-angle X-ray study of the IPN specimens show that there is modification of the heterogeneous structure of the network components as a result of the formation of the system. Firstly, qualitative differences are observed between the diffraction patterns of the original components and the IPN for most compositions studied. The diffraction curves for the IPN are more diffuse, and many curves show two intensity maxima, more or less clearly defined. A particularly marked difference is observed between the diffraction curves for the IPN containing small quantities of the ionomer and the scattering curve for the non-ionic form of polyurethane. It was suggested[43] that the introduction of small quantities of the ionomer into the polyurethane leads, during the production of the IPN, to the formation of micro-regions for which the periodicity of the distribution is determined by the microphase distribution of the polyurethane and the ionomer, leading to the production of the first maximum on the small-angle scattering curves. The second maximum is due to the effect of periodicity at the level of the blocks of different chemical character in the polyurethane. The maxima on the small-angle scattering curves for IPN with medium compositions are very poorly defined. This indicates that the periodicity at the level of the distribution of polyurethane and the ionomer and at the level of the flexible and rigid blocks is broken down to a considerable extent.

To obtain further information on the nature of the heterogeneity revealed in the IPN studied, the experimental values of $\Delta\bar{\rho}^{2\prime}$ were compared with the theoretically calculated $\Delta\bar{\rho}_c^2$ for different models of the heterogeneous structure.[43] Three models were used to calculate $\Delta\bar{\rho}_c^2$. The first model assumes a microphase distribution with the formation of polyurethane and the ionomer, within which there is complete blending of the flexible and rigid blocks. In contrast to the first model, the second model assumes complete distribution of the blocks of different character in the micro-regions of polyurethane and the ionomer. The third model, like the first two, assumes complete distribution of polyurethane and the ionomer, but unlike the first and second models it assumes that the micro-regions of polyurethane and the ionomer retain the degree of segregation characteristic of the individual networks. The calculations showed that the third model gives the best approximation for the description of the heterogeneous structure of the IPN.

When the third model is adopted, the $\Delta\bar{\rho}_c^2$ values are greater than $\Delta\bar{\rho}^{2\prime}$, particularly at high concentrations of the ionomer. This indicates that the micro-regions of the phase separation in real IPN are more "diffuse" than assumed by the third model. In other words, the IPN studied show a high degree of blending of polyurethane and the ionomer; this is generally characteristic of those cases where the separation of the phases during the production of the complex polymeric system stops at some intermediate stage. As in individual network polymers, the incomplete separation of the phases may be due to retardation of the movement of the molecular chains during the production of the three-dimensional structure.[22,44] The introduction of ionogenic groups into one of the components, leading to the formation of "ionic" cross-linkages, produces even greater retardation of the phase separation. These suggestions are confirmed by the results of morphological studies of ionomer-containing IPN given in the preceding section.

Thus morphological and X-ray diffraction studies of ionomer-containing IPN indicate that systems of this type have a complex structure with different levels of hetero-

heterogeneity at the level of the components and heterogeneity within each component at the level of the blocks of different chemical character and regions with different concentrations of ionogenic groups. As noted in Ref. 43, the formation of "diffuse" micro-regions of phase separation with a wide range of values of the degree of segregation of the components is possible, depending on the nature of the intermolecular interactions in systems of the given type and on the previous history of these systems.

## II. THERMODYNAMIC PROPERTIES

The introduction of ionogenic groups into one of the components of IPN, even when they are of similar chemical character, leads to thermodynamic incompatibility of the components in the IPN.[45] This has been demonstrated for IPN containing polyurethane and a polyurethane monomer; the composition dependence of the thermodynamic compatibility of the components was studied, the coefficients of self-diffusion of the solvent calculated, the fraction of the free volume and the change in it with change in the component ratio in the IPN determined, and the influence of the filler on the thermodynamic interaction at the interface examined.[45,46,47] The polyurethanes were based on the adduct of trimethylolpropane and tolylene di-isocyanate (TMP + 2,4-TDI) and a copolymer of propylene oxide and tetrahydrofuran[33] or polyoxytetramethylene.[45] The ionomers used were a polyurethane ionomer with a three-dimensional structure based on polyoxypropylene glycol (MM 3000), 2,4-TDI, 2-dimethylaminoethanol, and 1,5-dibromopentane[45] (ionomer A) or a linear ionomer based on polyoxytetramethylene, 2,4-TDI, and potassium dihydroxybenzoate[45] (ionomer B).

An analysis of the isotherms for the sorption of organic vapours by specimens of these IPN and the individual components made it possible to calculate the thermodynamic parameters. Thus the concentration dependence of the mean free energy of mixing of the solvent with the individual networks and the IPN, and the method proposed by Tager,[48] were used to calculate the change in the free energy of mixing of the polyurethanes and the polyurethane ionomers in the IPN. The results of the calculation are given in Fig. 2. $\Delta G_m$ is positive throughout practically the entire range of compositions, that is the components of the system are thermodynamically incompatible. The greatest separation into phases is observed for medium compositions (in the case of ionomer A) and at low concentrations of ionomer B in the polyurethane. An exception is the range corresponding to small quantities of added ionomer A, where $\Delta G_m$ is negative, that is the components are compatible. Compatibility in restricted ranges of this kind is observed for many heterogeneous systems.[49,50] The components of the polyurethane–linear ionomer (ionomer B) system, that is in the semi-IPN, are incompatible throughout the composition range (curve 2 in Fig. 2); the degree of incompatibility increases with increase in the proportion of ionomer. Thus even when the components of the IPN are very similar in chemical character, the introduction of ionogenic groups into one of the components leads to thermodynamic incompability of the components, producing the heterogeneity of the systems as a result of phase separation during the formation of the IPN.

As already noted, the interpretation of most experimental data on the properties of ionomers is based on the idea that multiplets and clusters are formed.[21] The ability of the ionomer to undergo association will probably have a significant influence on the phase separation processes in ionomer-containing IPN. The introduction of even small quantities of polyurethane into an ionomer with a linear structure[46] will apparently lead to a sharp increase in the degree of association of the latter. Polyurethane, added in small quantities, probably cannot form a continuous network, for the reasons examined in Ref. 51, and it will be distributed by diffusion as individual fragments in the bulk of the ionomer, facilitating self-association of the ionomer in the IPN system. Self-association of the ionomer B is also facilitated by its linear structure, which gives greater mobility of the segments (compared with the three-dimensional ionomer A) and leads to the formation of associates of ionic groups.

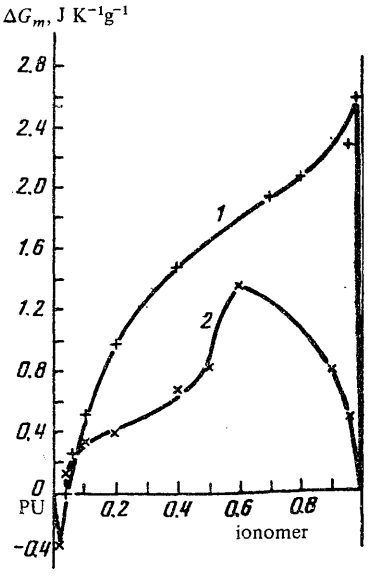



**Figure 2.** Composition dependence of $\Delta G_m$ for IPN based on polyurethane (PU) and ionomers A (1) and B (2).[45]

The self-association of the ionomer apparently intensifies the microphase separation in the IPN. As a result, the concentration dependence of the free energy of mixing of the components shows a maximum for small quantities of added polyurethane (see Fig. 2). At a higher concentration of polyurethane in the semi-IPN (medium compositions and the range of low concentrations of the ionomer in polyurethane), self-association is probably observed to a smaller extent, since the formation of the three-dimensional structure of the polyurethane, which is the matrix in these composition ranges, retards the process of phase separation in the IPN. The conditions of phase separation in these composition ranges are apparently close to those in IPN not containing ionomers.[52,53]

Microphase separation in the IPN leads to a redistribution of the free volume.[45–47] Quantitative treatment of data on the sorption of the vapours of substances with low molecular weight by IPN specimens using Fujita's theory[54,55] enabled the authors cited[45–47] to calculate the fraction of free volume in the ionomer-containing IPN.

The results are given in Fig. 3. For IPN containing the cation-active ionomer with a three-dimensional structure (ionomer A), at low concentrations of the components, the value of $f(T)$ is lower than the additive value, but for

intermediate compositions the IPN specimens show an increased proportion of free volume; for the IPN containing the anion-active ionomer (ionomer B), $f(T)$ deviates from the additive value towards higher values throughout the composition range, that is the IPN have a higher proportion of free volume.

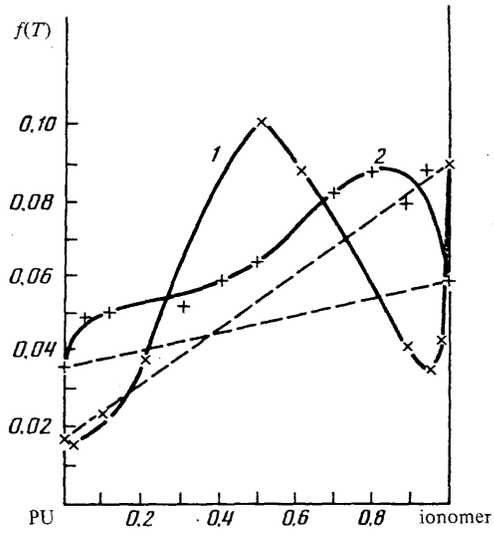



**Figure 3.** Dependence of the fraction of the free volume $f(T)$ on the component ratio for IPN containing ionomer A (curve *1*) and ionomer B (curve *2*); the broken lines give the additive relationships.[46]

Comparison of the concentration dependence of $f(T)$ and $\Delta G_m$ shows two common extremal points (curves *1* in Figs. 2 and 3), a minimum at low fractions of the ionomer A in the IPN, and a maximum at medium compositions, that is the compatibility range has a lower proportion of free volume than the individual components, and the range of greatest separation of the phases in the system corresponds to an excess of free volume. The self-association of the cation-active ionomer in the IPN system, leading to an increase in the segregation of the components in these systems, is apparently less marked than in the case of the anion-active ionomer (at least in the range of low concentrations of one of the components), since for the individual ionomers the formation of associates is more characteristic of the anion-active ionomers, as noted earlier. This is possibly due not only to the nature of the salt centres but also to the fact that ionomer A has a network structure, and ionomer B a linear structure. In this connection, phase separation accompanied by the formation of loose intermediate regions is more characteristic of the IPN with the linear ionomer (ionomer B),[3] leading to the production of an excess free volume throughout the composition range (curve *2* in Fig. 3).

The addition of a filler to the composition in the production of the IPN introduces its own characteristic features into the thermodynamic properties of these systems. Thus the introduction of small quantities (2–10%) of carbon fibres into IPN based on polyurethane and ionomer A leads to a decrease in their sorptive power;[47] the sorption decreases irregularly with increase in the concentration of the filler. This may be due to the competing action of two simultaneous processes: the formation of a more compact boundary layer and polymer–filler bonds, leading to a decrease in sorption, and the production of defects in the network (a decrease in the number of chemical nodes, "free" ends in the network) formed in the presence of the filler, leading to an increase in sorption.[51] Another noteworthy feature is that in the formation of two polymer networks in the presence of a filler for which the networks have different affinities, selective adsorption of one of the polymers will take place; this will lead to a change in the composition of the boundary layers in the final IPN structure produced, at the same time changing the extent of the sorption of the vapours of low-molecular-weight substances by the filled IPN.

For the case of a decrease in sorption in filled polymers compared with non-filled polymers, a thermodynamic cycle has been proposed[56] for estimating the extent of the reaction of the polymer with the filler.

$\Delta G^*_{p-f}$, that is the free energy of formation of the polymer–filler bond, which is a measure of the interaction of the polymer with the filler, is determined experimentally from the isotherms for the sorption of the vapours of organic solvents by the free polymer, the filler, and the filled polymer.[56] $\Delta G^*_{p-f}$ is calculated using the equation:

$$\Delta G^*_{p\text{-}f} = \Delta G_1 + n\Delta G_2 - \Delta G_3$$

where $\Delta G_1$ and $\Delta G_3$ are the free energies of the reactions of the polymer and the filled polymer with a large quantity of solvent, and $\Delta G_2$ the free energy of the reaction of the filler with a large quantity of the solvent.

Calculation showed[47] that for the polyurethane–carbon fibre system, the free energy of the polymer–filler interaction $\Delta G^*_{p-f}$ is negative in the range of filler concentrations studied. This indicates that the system is thermodynamically stable. For the polyurethane ionomer, only the composition with a low concentration (2%) of carbon fibres was found to be thermodynamically stable. Further increase in the filler concentration leads to destabilisation of the system, and the free energy becomes positive. Polymer–polymer contacts become energetically more favourable than polymer–filler contacts. Thus the ionomer macromolecules are less effectively adsorbed on the carbon fibres than the polyurethane macromolecules.

For filled IPN, the sign of $\Delta G^*_{p-f}$ depends on the component ratio at which the filler is introduced into the composition; at low concentrations of the ionomer (up to 10%) in the filled IPN, $\Delta G^*_{p-f}$ is negative, that is the system is thermodynamically stable; at an ionomer concentration of 30% or more, $\Delta G^*_{p-f}$ is positive, that is the system is destabilised. Here it is evidently necessary to take account of the influence of the filler on the microphase separation taking place during the formation of the IPN. According to the ideas developed in Ref. 5, in the formation of composite materials based on hybrid binders, the rate of the microphase separation and the degree of segregation in the hybrid binder depend on the reaction of the components with the filler. Thus if the filler reacts preferentially with one of the components, the rate of the microphase separation increases, and the degree of segregation should be greater. This probably takes place when carbon fibre is introduced into a polyurethane–polyurethane IPN containing 30% or more of the ionomer, where $\Delta G^*_{p-f}$ is positive. At low concentrations of the ionomer, in spite of a possible increase in the rate of the microphase separation under the influence of the filler, $\Delta G^*_{p-f}$ remains negative.

## IV. THE SWELLING OF IONOMER-CONTAINING INTERPENETRATING POLYMER NETWORKS

The swelling of ionomer-containing IPN obtained by sequential setting have been studied;[33,34,57] the ionogenic groups were introduced into one of the components of the IPN [57] or into both components.[33,34] The swelling of the IPN based on cross-linked polystyrene (network 1) and the copolymer of ammonium acrylate with ethyl acrylate (network 2) was carried out using toluene (a "good solvent" for network 1) and water (a "good solvent" for network 2). The experimental values of the swelling were compared with the values calculated using the additivity rule and assuming that the networks do not influence one another. All the IPN specimens studied undergo appreciable swelling in water and toluene, but to a much smaller extent (smaller by a factor of 3-6) than that calculated from the additivity rule. In the opinion of the authors cited, this behaviour indicates indirectly that both networks in the IPN system are continuous.[57]

Detailed studies have been made[33,34] of the swelling of cross-linked polystyrene, polyvinylpyridine, and IPN based on them, with and without ionogenic groups of different types; the anion-containing component of the IPN was obtained by sulphonation of the phenyl ring of polystyrene, and the cation-containing component by quaternisation of the pyridine ring by treating polyvinylpyridine with methyl fluorosulphonate solution.[33,34] The data on the swelling of the IPN and its components, not containing ionogenic groups, were analysed using the Flory–Rehner[58] and Thiele–Cohen[59] equations. The last equation was derived from the Flory–Rehner equation for application to homo-IPN, that is IPN based on two or more polymers of the same chemical character, so-called "Millar IPN".[60] The final form of the equation is

$$\ln(1-v_1-v_2)+v_1+v_2+\psi_s(v_1+v_2)^2=V_s(\nu_1)'(1/v_1^0)^{2/3}\times \times(v_1^{1/3}-v_1/2)-v_s(\nu_2)'(v_2^{0\,2/3}v_2^{1/3}-v_2/2) \quad (1)$$

where $\nu_1$ and $\nu_2$ are the volume fractions of polymers 1 and 2 in the swollen state, $\nu_1^0$ and $\nu_2^0$ the same in the non-swollen state, $\psi_S$ the molar volume of the solvent, $\nu_1'$ and $\nu_2'$ the density of cross-linking of polymers 1 and 2 in mole $cm^{-3}$, found from the Flory–Rehner equation, and $(1/\nu_2^0)^{2/3}$ a correction coefficient (front factor) for the change in the internal energy on swelling.

In the analysis of the data on the swelling of IPN not containing ionogenic groups, the experimentally determined values of the volume fraction of the polymer in the swollen IPN specimens, $\nu$, were compared with the values calculated from Eqn.(1), in which $\nu = \nu_1 + \nu_2$. It was concluded that in the IPN studied, in the swollen state at least, there is no additional chemical and physical cross-linking, which might have been expected on formation of the IPN. The addition of ionogenic groups to IPN based on polystyrene and polyvinylpyridine introduces its own characteristic features into the behaviour of the specimens on swelling. Thus for swelling in water at different pH values, the magnitude of $\nu$ (the maximum swelling) is greatest in weakly acidic or neutral media for all IPN compositions.[33] The value of $\nu$ increases with increase in the concentration of quaternised polyvinylpyridine, that is sulphonated polystyrene undergoes swelling to a greater extent than quaternised PVP. The addition of NaCl to water leads to different behaviour of the IPN, depending on their composition: specimens enriched in sulphonated PS, as before, give the minimum values of $\nu$ in neutral and weakly acidic media; specimens enriched in quaternised PVP give a maximum value of $\nu$ (that is minimum swelling) in these media. The observed differences in the swelling of ionogenic IPN, depending on the composition of the "solvent", are attributed to the shielding effect produced on the addition of, in this case, $Na^+$ and $Cl^-$ ions, which influence the electrostatic repulsion of the ions in the actual network.[33,60] Thus the introduction of ionogenic groups into the IPN makes it possible to vary the degree of interaction of these systems with the solvents over a wide range by changing the composition; this is important when IPN are used as ion-exchange resins and membranes.

From an analysis of the results of the study of the swelling of IPN specimens consisting of a copolymer of styrene with divinylbenzene (ST + DVB) and a copolymer of methacrylic acid with divinylbenzene (MA + DVB), an attempt was made[61] to obtain a criterion of the degree of interpenetration in IPN. The IPN indicated were obtained by sequential setting; specimens of the ST + DVB copolymer were first obtained, after which they were swollen in an MA + DVB monomer mixture, followed by polymerisation of the system. The IPN were obtained in the $H^+$- and $Na^+$-forms, and the swelling of the individual components and the IPN in a series of solvents was studied. Determination of the density of cross-linking from the swelling data showed that the experimental values of $\nu_e$ (the effective density of nodes in the network) of the IPN specimens are much greater than the values calculated from the additivity rule. From the assumption that the IPN is a heterogeneous system provisionally consisting of three phases (the phases of the individual components and the intermediate range), and an analysis of the swelling data, the following criteria for the degree of interpenetration in IPN were proposed:[61] 1) the difference between the sum of the specific volumes of the gels of networks 1 and 2 and the specific volume of the IPN gel

$$\Delta V = V_1\cdot v_1(1-P_1)+V_2\cdot v_2-V_i(1-P_i) \quad (2)$$

and 2) the difference between the volume fraction of the copolymer in the IPN gel and the sum of the volume fractions of the copolymers in the gels of networks 1 and 2:

$$\Delta v_g = v_{g_i}-(v_{g_i}\cdot v_1+v_{g_i}\cdot v_2) \quad (3)$$

where $V_1$, $V_2$, and $V_i$ are the specific volumes of networks 1 and 2 and the IPN, $\nu_1$ and $\nu_2$ the volume fractions of networks 1 and 2 of the IPN, $P_1$ and $P_i$ the porosities of network 1 and the IPN, and $\nu_{g_1}$, $\nu_{g_2}$, and $\nu_{g_i}$ the volume fractions of the copolymer in the gels of networks 1 and 2 and the IPN.

The proposed criteria, like Frisch's interpenetration criterion,[62] are applicable only when the number of nodes in the networks of the individual components is identical to that for the components in the IPN system; this is not observed in practice, since IPN are micro-filled systems,[3] to which all the ideas developed for filled polymers are applicable.[51] Thus the proposed interpenetration criteria can be criticised. The most appropriate criterion of the degree of interpenetration is apparently the degree of segregation, as noted above (see section II).

The fact that the experimental values of $\nu_e$ and the other parameters deviate considerably from the values calculated from the additivity rule for ionomer-containing IPN [61] indicates not only and not so much an increase in the degree of interpenetration in IPN, but also and more particularly the characteristic features of systems of this type determined by the increased self-association of the ionomeric component in the IPN system. This question will be discussed later.

## V. MECHANICAL AND RELAXATION PROPERTIES. TRANSITION TEMPERATURES

The study of the composition dependence of the mechanical properties of ionomeric IPN revealed the same regularity as for IPN of other types and mixtures of linear polymers, that is the extremal character of the change in properties with change in the component ratio. Thus an IPN consisting of polyurethane and a polyurethane ionomer[46] showed an extremal increase in the tensile strength at low concentrations (5%) of the polyurethane ionomer.[43] The breaking strain also showed an unexpected increase. An extremal change in properties with change in composition is a general regular feature of binary systems: mixtures of linear polymers, IPN, semi-IPN, and filled polymers. The reasons for this phenomenon are undoubtedly related to the characteristic features of the structural changes in the composites with change in their composition, but in spite of a number of attempts to explain the observed extremal values for different systems, no general explanation of these phenomena has yet been given.

The method of preparation of ionomer-containing IPN has a significant influence on their mechanical and relaxation properties. This has been demonstrated for thermoplastic IPN: chemically and mechanically blended IPN based on copolymers of styrene, ethylene, and butene (copolymer 1) and styrene, methacrylic acid, and isoprene (copolymer 2) (CBT IPN and MBT IPN respectively) differ in various mechanical properties. Both CBT IPN and MBT IPN with the ionomeric component in the acid form have lower strength values than IPN with the ionomeric component in the salt form.[40] When copolymer 2 is neutralised, the resulting more rigid component (the ionomer) acts as a characteristic filler for copolymer 1, leading to an increase in the mechanical strength of the IPN. CBT IPN have a higher tensile strength and a greater elongation at rupture, but a lower modulus of elasticity, compared with MBT IPN. This change in mechanical properties was related[18] to the morphology of these IPN; thus the lower modulus of elasticity of the CBT IPN was attributed to the greater degree of dispersion of copolymer 2 (the ionomer) in the matrix of copolymer 1.

The relaxation properties of the above systems have also been studied.[40,41] Data on the temperature dependence of the imaginary part $E''$ of the complex modulus $E^*$ established that the individual copolymer 1 has two glass-transition temperatures; the first, at −60 °C, is due to the presence of blocks of ethylene and butene, and the second, at 102 °C, is due to glass formation by the styrene blocks. The ionomer shows one glass-transition temperature at 140 °C. These three glass-transition temperatures also appear on the curves giving the temperature dependence of $E''$ for CBT IPN, without any deviations; this indicates that there is little blending at the molecular level of the components in the systems considered, in contrast to polyurethane–polyurethane ionomer systems,[43] discussed above.

The mechanical properties of these IPN have been described using the theoretical models of Takayanagi, Budyanskii, Davis, and Kerner.[40] The experimental data are most accurately described by Davis' equation, which assumes that both phases in the two-phase system are continuous. For MBT IPN, continuity of both phases is probably more characteristic, since Davis' equation provides a better description of the mechanical properties for MBT IPN than for CBT IPN. This correlation is illustrated directly by the electron microscope data given in the previous section, which show "double" continuity of the phases.

Systems related to ionomer-containing IPN are those in which one of the components is a polyelectrolyte such as acrylic acid and its derivatives. These systems[63] and their relaxation properties have been studied. They are IPN and semi-IPN based on polyoxyethylene (POE) and polyacrylic acid (PAA), obtained by sequential setting. Polyoxyethylene with a molecular mass of 7800–9000 was dissolved in a mixture of the monomer, a cross-linking agent (DVB), and an initiator (benzoyl peroxide), after which the polymerisation was carried out. This gave semi-IPN. The complete IPN were obtained by swelling the previously cross-linked POE in a mixture of the monomer and the cross-linking agent, followed by polymerisation. Study of the dynamical mechanical properties of the semi-IPN and total IPN obtained showed that the curves giving the temperature dependence of $E''$ and $\tan\delta$ for specimens with medium compositions or compositions close to them have a single maximum, indicating that there is one temperature transition in systems of this kind. Thus the specimens studied consist of single phases. For specimens in which PAA predominates, and in particular for the semi-IPN with 75 mass % PAA, two maxima are observed; one corresponds to that for the IPN with the equimolar component composition, and the other corresponds to the glass-transition temperature of PAA. For the complete IPN with approximately the same composition, a sharp second maximum is not observed; the curve shows only a slight shoulder. For semi-IPN and IPN enriched in POE, one broad transition is observed, with a maximum at a temperature slightly below the melting point of POE.

These results are interpreted in terms of the formation of complexes between POE and PAA molecules as a result of the production of hydrogen bonds between the COOH groups of the acid and the oxygen atoms of POE.[63]

The question of the association of PAA and POE during the polymerisation of acrylic acid in the presence of POE was examined earlier[64–66] by one of the authors of Ref.63. It is suggested that dynamic mechanical analysis shows that the formation of a single-phase system in IPN and semi-IPN with medium compositions and compositions close to them is due to complex formation. IPN with a low concentration of PAA, according to Ref.63, show microphase separation of POE domains and domains of POE + PAA complexes; IPN with a high PAA concentration show microphase separation of domains of PAA and the complexes. The degree of microphase separation or segregation is greater for the semi-IPN than for the complete IPN, and this is attributed to preliminary cross-linking of the POE during the preparation of the complete IPN. The interpenetration of the components and the formation of interpolymer complexes probably also explains the decrease in the crystallinity of POE in the system of semi-IPN and complete IPN.[63]

Analysis of the strength properties of IPN based on POE and PAA [63] or on polymethacrylic acid[67,68] revealed a characteristic feature of systems of this kind, of practical importance: for low mechanical strain, considerable elongation of the IPN specimens is observed, due to the possible dissociation of the POE + acid complexes and their rearrangement under the influence of the strain.

The characteristics of the reaction between the components and the molecular mobility in IPN based on polymers of related character (polyurethanes) have been studied.[69] NMR spectroscopy was used to study the temperature dependence of the second moment of the absorption line $\Delta H_2^2$ for IPN based on polyurethane (PU) and a polyurethane ionomer (PUI). The latter was obtained by the reaction of oligotetramethylene glycol, TDI, and sodium dihydroxybenzoate.

The curve giving the temperature dependence of $\Delta H_2^2$ for PU showed three main transitions: transition I in the low-temperature range (−130 °C) due to the defreezing of the molecular mobility of the methyl groups:[70] transition II, which begins at −90 °C and is due to the retarded rotation of the methylene groups; and transition III at −10 °C,

apparently due to the start of the segmental movement of large parts of the molecules,[71] possibly sections of the polyurethane chains between the transverse cross-linkages. Unlike PU, the PUI does not show sharply defined temperature transitions: $\Delta H_2^2$ decreases gradually with increase in temperature. For the IPN specimens, transitions I and II are preserved, but transition II is displaced to lower temperatures with change in the ionomer concentration. Transition II, observed at low concentrations of the ionomer, becomes "blurred" with increase in the quantity of the latter.

The preservation of the IPN of the transitions characteristic of the individual components indicates that two phases are present, in spite of the similarity in the chemical character of the components. In the two-phase system there may be intermolecular interactions of different kinds between the components. The nature of the interaction between PU and the PUI in the IPN was therefore estimated from the magnitude of $(\Delta H_2^2)_{int}$, determined as follows:

$$(\Delta H_2^2)_{int} = (\Delta H_2^2)_{expt} - (\Delta H_2^2)_{theor}$$

where $(\Delta H_2^2)_{theor}$ is the second moment of the absorption line of the two-component system, calculated from the additivity rule. The quantity $(\Delta H_2^2)_{int}$ may take positive or negative values if there is an intermolecular interaction between the components of the system, in spite of the absence of chemical transformations. In the absence of interactions, $(\Delta H_2^2)_{expt} = 0$. Calculations showed that the values of $(\Delta H_2^2)_{int}$ for all IPN specimens at the lowest temperature used (−130 °C) are negative, indicating that the molecular mobility of the IPN is greater than that of the individual components. The study of the thermodynamic compatibility of the components in IPN of this type (see section II) showed that the components are incompatible (the free energy is positive). Thus the system studied, like non-ionogenic IPN, shows separation of the phases during its formation, leading to the production of an intermediate range, which, as in non-ionogenic IPN, has a loose structure, as indicated by the negative values of $(\Delta H_2^2)_{int}$.

Calculation of the activation energy of the transitions in the IPN and its components showed that the value of the activation energy $E$ changes non-additively and irregularly with change in composition. For non-ionogenic IPN, the value of $E$ for the transitions also changed irregularly with change in composition; for all IPN specimens, however, the value of $E$ was always less than the additive value and less than the values for the individual components;[72] this was attributed to the formation of a loose intermediate range, facilitating molecular movement in it. In ionogenic IPN, the value of $E$ is lower than the additive value only for IPN specimens containing up to 20–30% of the ionomer. At high concentrations of the ionomer, $E$ is greater than the additive value.

These results were interpreted[69] using the theory of multiplet and cluster formation in ionomers, developed in a number of studies.[6,21,73,74] The ability of the ionomer in the IPN to undergo self-association possibly intensifies the microphase separation. At the same time, the formation of a loose intermediate region, having an excess free volume, facilitates the self-association of the ionomeric component in the IPN system, compared with the individual ionomer. The association of the ionogenic groups is probably the decisive factor in the change in molecular mobility in the IPN when it contains ionomer concentrations of 20–30%, so that $E$ is greater than the additive value. At lower concentrations of the ionomer, when the matrix is PU, the self-association of the ionomeric component is not so marked, and the molecular movement in the system is determined chiefly by the existence of the intermediate range. In this case $E$ is lower than the additive value.

A study of the temperature transitions in an epoxide resin–polyurethane ionomer system (based on polyoxypropylene glycol, TDI, dimethylaminoethanol, and dibromopentane) [75] showed that for IPN of all compositions, two transitions are observed, lying in the region of the glass-transition temperatures of the component networks. In the IPN, however, the glass-transition temperatures are displaced along the temperature scale, as indicated in Fig. 4. The temperature of the transition, which is due to the glass transition of the epoxide resin (curve *1* in Fig. 4), in the IPN changes with change in composition along a curve which has two minima at concentrations of each component of about 10%. The second transition, which lies in the negative temperature range and is due to the glass transition of the polyurethane ionomer (curve *2* in Fig. 4), is displaced to higher temperatures with increase in the proportion of resin in the IPN.

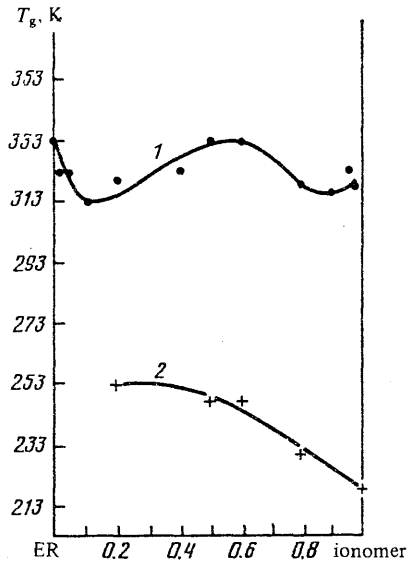



**Figure 4.** Change in the glass-transition temperature with change in composition for IPN based on polyurethane and epoxide resin (ER): *1*) glass-transition temperature of the epoxide resin, *2*) glass-transition temperature of the polyurethane ionomer.[75]

The results were interpreted[75] in terms of the degree of completeness of the processes of microphase separation and the degree of segregation. At a low degree of segregation, leading to the formation of an appreciable proportion of interphase regions, as in the case of blending at the molecular level, the temperature transitions characteristic of the individual components may not be observed.[76] The presence of two glass-transition temperatures in the IPN indicates, however, that there is a fairly high degree of segregation of the components even at low concentrations of each of them. In the range of medium concentrations, however, where the glass-transition temperature of the epoxide resin in the IPN is approximately equal to that for the pure epoxide resin, the degree of segregation is probably very high, and the phase separation is extensive.

Thus the formation of ionic "cross-linkages" in IPN as a result of the introduction of ionogenic groups into one of the components has a significant influence on the mechanical and relaxation properties. This is apparently related to the increase in the degree of segregation of the components of the system due to the increase in the association of the ionogenic groups in the IPN compared with the pure ionomer. The association of the ionogenic groups is also possibly responsible for the marked difference between the experimental and theoretical values of $\nu_e$ (see section III), as follows from Ref. 61; the associates of ionogenic groups are characteristic nodes of the network, leading to an increase in $\nu_e$.

The question of the formation of multiplets and associates in individual ionomers of different character is still being discussed in the literature. Analysis of the results of studies in this field indicates that the nature of the ionogenic groups has a decisive influence on the association: associates are detected for polymers of different classes with anion-containing ionomers; associates are less frequently detected in cation-containing ionomers. This field is now being intensively studied.[6,20]

## VI. ADHESIVE PROPERTIES

Adhesives and coatings based on IPN show good adhesion to supports of different kinds;[3,4] no systematic studies of the adhesive properties of these coatings, or of coatings based on ionomer-containing IPN, have been described, however. The use of an ionomer as one of the components of the IPN to obtain adhesives and coatings will apparently make it possible to obtain materials with good adhesive power and low hydrophilic character (compared with the individual ionomers).

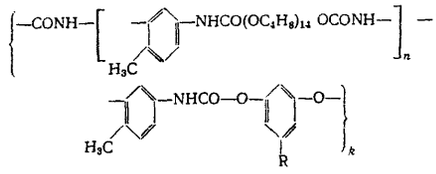
Influence of the nature of the counter-ion and the concentration of salt groups on the adhesive strength (N $m^{-1}$) of coatings on substrates of different character*.

| Type of salt | Steel | | | Glass | | |
|---|---|---|---|---|---|---|
| | $n$=1 | $n$=2 | $n$=3 | $n$=1 | $n$=2 | $n$=3 |
| Lithium salt | 340 | 220 | 180 | 280 | 210 | 140 |
| Sodium salt | 280 | 200 | 170 | 230 | 160 | 130 |
| Potassium salt | 220 | 200 | 100÷95 | 210 | 180 | 130 |

| Type of salt | Dural | | | Brass | | |
|---|---|---|---|---|---|---|
| | $n$=1 | $n$=2 | $n$=3 | $n$=1 | $n$=2 | $n$=3 |
| Lithium salt | 220 | 170 | 95 | 320 | 240 | 220 |
| Sodium salt | 160 | 140 | 100 | 310 | 180÷200 | 200÷220 |
| Potassium salt | 90 | 120 | 75 | 212÷200 | 180 | 110 |

*Temperature of formation of the coatings 80 °C.

The adhesion to various supports (steel, brass, glass, Dural) has been studied[77] for coatings based on IPN consisting of network polyurethane and polyurethane ionomers with the general structure



where $n$ = 1, 2, 3; $R$ = COOLi, COONa, COOK; and $k$ is the degree of poly-addition. The study of the influence of the concentration of salt groups in the chain of the ionomers studied on the strength of the adhesion (at separation) showed that increase in the concentration of salt groups in the structure of the polymer chain (that is decrease in $n$) increases the adhesive strength of the ionomeric coatings for all supports studied (see Table). The fact that a significant increase in the adhesive strength of the ionomers is observed only at a high concentration of salt groups in the composition makes these polymers unsuitable as protective coatings, because of their highly hydrophilic nature; their use as one of the components of the coating gave good results, however.[71]

Fig. 5 gives typical curves showing the change in the equilibrium work of adhesion for coatings based on ionomer-containing IPN with change in composition. At low concentrations of each component, an extremal increase in adhesion is observed; this is particularly clearly defined at low concentrations of the ionomer. At the same time, the coatings are only slightly hydrophilic, and this is important from the practical viewpoint. The extremal point on the graph giving the dependence of the hydrophilic character on the concentration composition of the IPN probably corresponds to the range of concentrations at which the ionomeric component becomes the continuous phase.

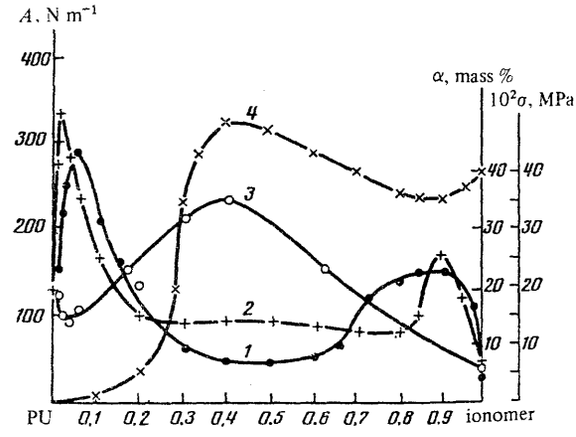



**Figure 5.** Dependence of the quasi-equilibrium work of adhesion $A$ (*1*, *2*), hydrophilic character $\alpha$ (*3*), and internal stresses $\sigma$ (*4*) on the component ratio.[77]

In the production of coatings, the influence of the solid surface of the support is superimposed on the process of IPN formation, that is selective adsorption of a particular component on the surface is possible, leading to an irregular distribution of the components in the boundary layer of the coating. Thus analysis of the surface tension values, and also data on the temperature dependence of the adhesive strength of the above coatings, indicated[77] that the polar groups of the ionomeric component are oriented on the surface of the substrate, leading to an increase in the adhesion of the coating. The principal feature of the dependence of the strength of adhesion on the composition of the IPN, however, is the presence of extremal points.

Up to a certain composition, the microregions of one of the components, distributed in the matrix of the other component, apparently act as a reinforcing filler, leading to an

improvement in various characteristics of the materials based on IPN, in particular the adhesion of coatings. In the range of medium and similar compositions, however, inversion of the phases is observed, that is the component acting as the micro-filler gradually becomes the matrix; in this range there is generally a deterioration in both the mechanical and the adhesive properties (see curves *1* and *2* in Fig.5). The gradual transformation of the filler component into the matrix component produces strained structures, as indicated, for example, by the marked increase in internal strain in the coatings (curve *3* in Fig.5). This in turn leads to a decrease in the strength of adhesion.

Thus the use of an ionomer as one of the components in the production of coatings based on IPN makes it possible to obtain coatings whose adhesive strength is considerably greater than that of the individual components. A more detailed explanation of the reasons for this phenomenon requires further studies on a wider range of systems.

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The above analysis of published data indicates that the introduction of ionogenic groups into IPN systems leads to a significant change in the mechanical, structural, and relaxational properties of materials based on these IPN. In contrast to non-ionogenic IPN, where a change in properties is achieved only by varying the component ratio in the system, in the case of ionomer-containing IPN it is possible to vary the properties of the materials obtained more widely by changing the quantity and nature of the salt groups in the ionomeric component of the IPN. Information on the preparation and study of ionomeric IPN began to be published only in the last 5–7 years. Reports indicate,[78] however, that studies in this field are being extended; the synthesis of new IPN with ionogenic groups in both components, with opposite charges, is being suggested. Methods are being developed for obtaining IPN in which interpolymer complexes are formed.[67,68]

The use of polymers of more complex chemical character with active groups in the chains as components of IPN naturally complicates the production of the system, and alters its final properties considerably. A comparative study of IPN consisting of polymers of the same chemical character with and without ionogenic groups has not yet been carried out, however. Nevertheless, judging from the above results of structural studies of ionomer-containing IPN, the conditions of the chemical reactions, and also the conditions of microphase separation, in these systems will differ from those in non-ionogenic IPN. The task of the immediate future is to carry out studies in these directions.

Thus ionomer-containing IPN represent a new type of hybrid binder, whose use will make it possible to develop more complex combinations of different polymer structural states and to create new possibilities for controlling the physicomechanical properties of polymeric materials based on them.

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